(4)

CHEMICAL
RESEARCH,
DEVELOPMENT &
ENGINEERING
CENTER

CRDEC-CR-086

A VAPOR CHALENGE MEHTOD OF MEASURING THE RESIDUAL LIFE OF GAS FILTERS

Thomas W. Mix
Terence C. McDonald

MERIX CORPORATION
Needham Heights, MA 02194

August 1990

U.S. ARMY
ARMAMENT
MUNITIONS
CHEMICAL COMMAND

Aberdeen Proving Ground, Maryland 21010-5423

90

Disclaimer

The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

Distribution Statement

Approved for public release; distribution is unlimited.

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	1990 August	Final, 86 Aug - 89 Jun

4. TITLE AND SUBTITLE
A Vapor Challenge Method of Measuring the Residual Life of Gas Filters

5. FUNDING NUMBERS
C-DAAA15-86-C-0081

6. AUTHOR(S)
Mix, Thomas W., and McDonald, Terence C.

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Merix Corporation
77 Charles Street
Needham Heights, MA 02194

8. PERFORMING ORGANIZATION REPORT NUMBER
CRDEC-CR-086

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
CDR, CRDEC, ATTN: SMCCR-PPC, APG, MD 21010-5423

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES
COR: Robert W. Morrison, SMCCR-PPD, (301) 671-5689

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

A residual filter life test has been developed involving the use of a weakly adsorbed vapor to "count" available adsorption sites. The method was developed for military filters containing ASC carbon to determine when the physical adsorption capacity of a filter had been depleted to the extent that change-out is required. The procedure requires measurement of the time for a challenge chemical (ammonia) to appear in the filter effluent with a correction factor being applied based on the temperature and relative humidity of the airflow through the filter. The procedure is best suited for collective protection filters but could also be applied to gas mask canisters. A correlation between breakthrough time and residual adsorption capacity must be experimentally determined for each filter design. Work remains to be performed to demonstrate the test procedure on an actual filter system and to determine the correlation for each type of filter.

14. SUBJECT TERMS
-Agent
Chemical
ASC whetlerite
Gas filter

15. NUMBER OF PAGES
91

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

Blank

PREFACE

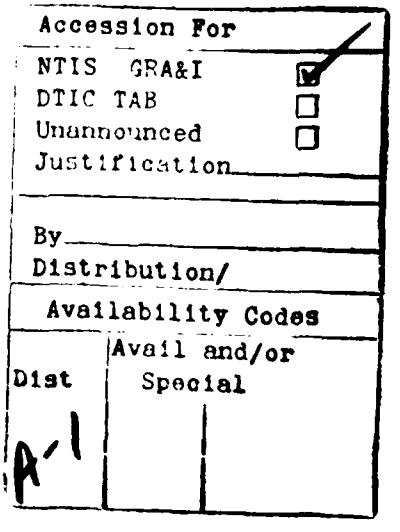
The work described in this report was authorized under Project No. DAAA15-86-C-0081, A Vapor Challenge Method of Measuring the Residual Life of Gas Filters. This work was started in August 1986 and completed in June 1989. The experimental data are recorded in laboratory notebooks 054-1, 054-2, 054-3, and 054-4 located at Merix Corporation (Needham Heights, MA).

The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

This report has been approved for release to the public.

Acknowledgments

The authors gratefully acknowledge the support and assistance provided by Robert Morrison and Thomas Lynn at CRDEC.



Blank

CONTENTS

LIST OF FIGURES

LIST OF TABLES

A Vapor Challenge Method of Measuring the Residual Life of Gas Filters

1. BACKGROUND

Since the introduction of chemical agents onto the battlefield in World War I, activated carbon filters have been used to provide protection against the inhalation of agent vapors. Activated carbon physically adsorbs the less volatile agents from the air, while metal impregnants on the carbon react with the more volatile, weakly sorbed agents. As they are currently prepared, ASC Whetlerite activated carbon filters are capable of protecting against all chemical agents. However, all carbon filters, including ASC Whetlerite filters, have a finite protective capacity. If the physical sorption capacity is exhausted through the adsorption of strongly bound materials, the filter will no longer protect against strongly sorbed agents. If the metal impregnants are consumed by reaction with agents or deteriorate over time through contact with atmospheric moisture, weakly sorbed agents will be able to penetrate the filter. And if rough handling causes channeling in the filter, agents will infiltrate through these cracks, even if the carbon itself has additional capacity.

Currently, there is no way for field personnel to determine when their filters need replacement, or what fraction of the original protective capacity of their filter remains intact. Without a residual filter capacity measurement, filters must be replaced prematurely, when it is certain that they are still good. This creates both an extra expense for more filters, and an additional burden on the filter supply and distribution system.

2. PREVIOUS WORK

Most of the previous attempts to measure residual filter life can be separated into two groups: gas pulse methods[1,2,3] and probe-in-bed methods.[4,5,6] In the gas pulse approaches, the filter is challenged with a known concentration of test gas, and the rate at which it penetrates through is measured. Premature penetration indicates that channeling has occurred, or that strongly sorbed materials have reduced the adsorptive capacity of the filter. And if the test gas can react with the metal impregnants, the concentration of reaction products in the effluent stream can indicate the residual filter reactivity. In the probe-in-bed methods, a detection device is placed within the filter, near the exit. When the probe detects the presence of agent, or other strongly adsorbed material, it warns the user that the filter capacity is nearly exhausted. Each approach has its own advantages. The gas pulse methods do not require any modification to the filter. They test the entire bed cross sectional area, detect channeling, monitor the activity of the metal impregnants, measure the fraction of residual filter capacity, and indicate when the filter is near exhaustion. Probe-in-bed methods are capable of distinguishing agents from other strongly sorbed materials, constantly monitor the filter while it is operating, and do not require a special testing procedure. And if

the filter is modified, they can also test the entire bed cross sectional area.

However, despite their promise, both gas pulse and probe-in-bed methods have had serious technical and practical difficulties which have prevented their use in the field. Gas pulse methods require the use of a volatile, lightly sorbed test gas to reduce the testing time. Generally, a low molecular weight, hydrophobic gas (methane, ethane, ethylene, acetylene, propane, carbon dioxide, bromobutane, sulfur hexafluoride, and Freons F-11, F-12, F-21, F-112 and F-113 have been utilized) is used as the test gas; these material break through rapidly, do not chemisorb or break down, and are relatively non-toxic. Unfortunately, adsorbed moisture on the bed, which does not compromise the protective capacity of the filter, can drastically affect the breakthrough time of the test gases. Probe-in-bed methods, which sample at a point, can not detect channeling unless the filter is modified, and do not measure the loss of filter reactivity. The introduction of the probe into the filter can itself provide a channel for agent penetration. And there is no single probe available which can detect all the materials which might penetrate the bed at the minimum required sensitivity level.

Among the practical difficulties, the primary one is the cost of the detection equipment. Gas pulse methods generally require a gas chromatograph to separate the test gas from other atmospheric constituents, and some sort of physical detector, such as a thermal conductivity detector or a flame ionization detector, to recognize the presence of the test gas. Probe-in-bed methods also require expensive detection devices. Other barriers to fieldability include the size, weight and fragility of the detection equipment, sensitivity of the calibration and measurements to extremes of temperature and humidity, and the requirement for trained personnel to conduct the tests. Given all these difficulties, Baker and Poziomek concluded in 1972 "that at this writing, there is not available any wholly satisfactory method for sorbent-life determination."[7]

3. MERIX APPROACH TO RESIDUAL FILTER LIFE MEASUREMENT

Given that most of the practical objections to the gas pulse and probe-in-bed filter life measurements are related to the expensive and unwieldy detection equipment, Merix has investigated replacing the equipment with simple, inexpensive, prepackaged, colorimetric, chemical reactions. In Phase I work, Merix conducted extensive tests on the direct colorimetric detection of agents penetrating through an ASC Whetlerite bed. It was concluded that while it was technically feasible to detect the agents, an impractically large number of reactions would have to be conducted to detect all possible agents. Therefore, in the phase II work, effort was focused on the gas pulse method. It was postulated that if a challenge substance could be found which would penetrate through the bed rapidly, was unaffected by adsorbed moisture, and could be detected by colorimetric reaction, a fieldable residual life test could be developed. Phase II work then focused on selecting a suitable challenge substance candidate, testing it under various conditions of temperature, relative humidity, and filter contamination which might be found in the field, and

then evaluating the potential of the method for a residual life measurement test.

4. EXPERIMENTAL WORK

4.1. Challenge Substance Selection

A challenge substance having the following characteristics was sought:

1) Under normal filter flowrate conditions, it will penetrate through a new filter in less than 10 min

Strictly speaking, this condition is both ambiguous and unnecessary. It is ambiguous because the breakthrough time through a filter depends not only upon the type of challenge substance, but also its concentration, the method used to introduce it into the inlet stream (pulse, square wave, step change), and other factors (temperature, adsorbed moisture, etc.). It is unnecessary in that the limiting time is that for penetration through an exhausted filter. So long as this breakthrough time is rapid, and the breakthrough time of a fresh filter is significantly longer, the exact value is irrelevant.

However, this criterion is included for four reasons. First, it correctly implies that the test conditions will be the same as the normal operating conditions. To do otherwise, would increase the complexity of the test, and provide a less direct measurement of filter performance under actual operation. Second, it provides a guideline for determining the test substance concentration and introduction method once the substance has been selected. Third, it places a reasonable limit on the total test time if a value for residual capacity is being measured. And finally, breakthrough time for a fresh bed is a value which might reasonably be reported in the literature; breakthrough times for partially exhausted beds probably would not be available.

2) Under normal filter flowrate conditions, it should have a critical bed depth of less than 20% of the filter thickness-

Critical bed depth refers to the thickness of filter required to reduce the test substance concentration from its inlet value to the maximum permissible outlet value. The test substance will immediately begin penetrating any filter thinner than this; it will also immediately penetrate any filter which has enough strongly bound contaminants adsorbed onto the front of the bed to reduce the remaining effective carbon thickness to less than the critical value. It is therefore impossible to use test substance breakthrough time to distinguish between a completely exhausted bed, and one which still has effective carbon in a less than critical bed depth thickness. Consequently, the filter must be discarded prior to complete exhaustion. Specifying a maximum critical bed depth will minimize the amount of wasted carbon.

3) It must be water soluble-

Since the amount of adsorbed water on the carbon can not be controlled, the tracer must be insensitive to moisture. Experiments have shown that while adsorbed atmospheric moisture can drastically decrease the retentivity of water insoluble vapors, it does not as strongly affect chemicals which are miscible with water.[8]

4) It must be easily detectable by colorimetric reaction or by an inexpensive probe-

A key to making the test practical is to use a simple, inexpensive detection method. If a colorimetric reaction is used, it should be able to detect the test substance at low concentrations, with minimal interference from any other chemical species which might reasonably be present. It should use reagents which are stable over time and over a range of temperatures. Ideally, the reaction should require just premixing of reagents and the presence of the test substance to develop a color; if possible, reactions requiring timing or the addition of developer reagents should be avoided. If an inexpensive, robust sensor is used as the detection method, it should also detect the test substance at low concentrations, with minimal interference from any other chemical species which might reasonably be present.

5) It must be stable to ASC Whetlerite-

The test substance should not break down or react with other substances adsorbed on the filter. Reactions with the metal impregnants should also be avoided; while such reactions could result in a future test of the impregnant activity, at present it is an undesirable complication.

6) It must have low toxicity and good warning properties-

At the concentrations used for residual life testing, the challenge substance should be non-toxic or of low toxicity. It should possess good warning properties (odor, lacrimator, etc.) at levels below any toxicity thresholds to prevent accidental overexposure during testing. Since the challenge substance will desorb off the carbon bed at low concentrations for a short time after the test, it should have no chronic toxicity.

Given these criteria, a literature search was conducted for likely challenge substance candidates. In the Division 10 report, ammonia, nitric oxide and carbon monoxide were identified as three gases which could rapidly penetrate through ASC Whetlerite filters; the report also indicated that acids and acid forming gases, and readily oxidized gases, such as arsine, would react with the metal impregnants.[9] Juhola and Friel estimated the breakthrough times of 900 common chemicals through the XM-41 ASC Whetlerite filter, at 37.8 ^{o}C, at inlet concentrations of either saturation or 2%, whichever was less.[10] Ammonia, nitric oxide and carbon monoxide all had estimated breakthrough times of about 4 minutes; examination of other substances indicated that there were 258 other chemicals which would penetrate in approximately 4 minutes. The report indicated that chemical vapor pressure was the primary factor in determining breakthrough time. All listed substances with vapor pressures

greater than 19 mmHg broke through in 4 minutes or less; none of those with vapor pressures less than 13 mmHg penetrated in less than 4 minutes.

Despite the apparent wealth of possible challenge substance candidates, it was unclear how many would still penetrate rapidly at a lower temperature and inlet concentration. The report suggested that substances which have a greater than atmospheric vapor pressure would penetrate most rapidly; 66 of the 258 possibilities are gases at 37.8 ^{o}C. Of these, three are gases normally found in the atmosphere, four are chemical agents, eight are acid gases, and eight are hydrophobic, aliphatic hydrocarbons. Of the remainder, at least two are liquids at room temperature.

At this point, the search was widened. The Handbook of Chemistry and Physics was used to identify all substances with boiling temperatures of less than 0 ^{o}C[11]. It listed 72 organic chemicals and 66 inorganic chemicals which met this requirement; of the 66, 29 were listed as decomposing in water, and were eliminated from further consideration. From the remaining 109 chemicals, the following types of chemicals were eliminated:

- challenge gases which have been tried previously, and found to be sensitive to adsorbed moisture. Acetylene, which seems to have the highest water solubility (approximately 20 times greater than ethane), has been left on the list for comparison purposes;
- noble gases, which can not be detected by colorimetric reaction;
- acid gases, and other chemicals, which would react with the metal impregnants;
- all chemicals which are unstable, or would react with moisture on the carbon;
- all chemicals listed as insoluble in water;
- all chemical agents;
- all perhalogenated aliphatic hydrocarbons, which are both insoluble in water, and do not readily react; and,
- all chemicals with water solubilities less than acetylene.

The remaining 36 candidates are presented in Table 1.

For 28 of the candidate challenge gas materials, there is no information about water solubility; by inspection, it was concluded that these materials are probably not very water soluble. Of the remaining eight, four have solubilities similar to acetylene. While the literature has not specifically stated that water adsorption interferes with acetylene adsorption, it has been tried previously and apparently not been successful. The remaining four candidate challenge gases, each 10 to 1000 times more soluble in water than acetylene, are listed in Table 2, and are each discussed in detail, below.

Methyl ether-

Of the four gases, methyl ether is probably the least toxic; while no exposure limits have been set for it, the values for the analogous diethyl ether are TWA=400 ppm and IDHL=19,000 ppm. It is also not noted for being noxious or irritating, although in 50% concentrations it is distinctly suffocating.[12] However, its other drawbacks outweigh this advantage. It is the least water soluble of the four gases, which would probably make it most sensitive to adsorbed moisture. It is chemically unreactive, and not easy to detect by a simple colorimetric reaction without heating. And it is highly flammable, with a lower explosive limit of 3.4%, and may form peroxides during storage. For these reasons, it was not considered further in this work.

Formaldehyde-

In contrast to methyl ether, formaldehyde is extremely reactive, and easily detected by colorimetric reactions with:

- chromotropic acid;
- J-acid;
- metal precipitation from nickel dimethylglyoxime; or
- metal precipitation from silver chromate.[13]

It is also much more water soluble. However, it has a major drawback which makes it unsuitable for this work: it can polymerize. If this were to occur on the carbon surface, it would both increase the measured formaldehyde breakthrough time in an unpredictable manner, and possibly block the carbon surface for an indefinite period. Polymerization would also prolong the period of formaldehyde desorption from the bed. Formaldehyde can be detected at concentrations below 1 ppm; it produces mild irritation at 2-5 ppm and becomes intolerable above 25 ppm[14]. Since formaldehyde is noxious at low concentrations, it might produce an extended period where the filter is unusable. Apart from its acute exposure effects, formaldehyde will sensitize a certain fraction of people to subsequent exposure. And in 1987, the EPA indicated that it was a probable carcinogen.

Methyl amine-

Like formaldehyde, methyl amine is extremely water soluble, and easy to detect by colorimetric reaction. It is also irritating at low concentrations (although less so than formaldehyde). Unlike formaldehyde, methyl amine does not seem to sensitize personnel, or cause any long term health effects;[15] with a short testing time and rapid desorption from the filter, exposure will be minimized. For this reason, it is considered a good choice for the challenge gas. However, it does not seem that methyl amine will behave in a qualitatively different manner from ammonia. Consequently, most experimentation was done with an ammonia challenge gas.

Ammonia-

Ammonia seems to have the best combination of physical, chemical and toxicological properties to meet the requirements of a challenge gas. It is volatile, and readily penetrates through a fresh carbon bed. It is highly water soluble, and easily detectable, either by an acid/base indicator reaction or a pH probe. While ammonia is acutely hazardous, it is less toxic than either formaldehyde or methyl amine, and has a distinctive odor well below its IDHL level. Relatively high doses of ammonia can be tolerated for the short periods of time involved in testing; it has been reported that exposures up to 5000 ppm of ammonia for 5 min caused no deaths in humans.[16] Moreover, because ammonia is metabolized by the body, there should be no long term effects of exposure.

From a practical standpoint, ammonia has several other desirable features. Because it is an important chemical, there is a wealth of literature about its physical and chemical properties as both a pure substance and a water solution. It adsorption properties on ASC Whetlerite have also been studied. It is widely available as a gas, gas mixture, and a water solution for use in experimentation, and its penetration through a test bed can be detected by colorimetric reaction, pH meter, or gas chromatograph with a thermal conductivity detector.

The one drawback of ammonia is its potential reactivity with the metal impregnants on the carbon. Silver, copper and chromium ions can all form complexes with ammonia in solution. In addition, like most organic chemicals, ammonia can react with the strong oxidant CrO_3. Both gaseous ammonia and aqueous solutions have been observed to react very exothermically with CrO_3.[17] However, at the ambient temperatures and low ammonia concentrations which would be used in the residual life test, ammonia is not expected to react with the metal impregnants. Previous work has demonstrated that, in small quantities, ammonia does not reduce CrO_3 impregnated on activated carbon from Cr^{+6} to Cr^{+3} at temperatures below $150^{o}C$. In fact, ammonia increases the capacity of the impregnated carbon for HCl.[18]

4.2 Experimentation With Ammonia

All the carbon loading and breakthrough time experiments conducted in the Phase II program were "minican" tests. In these tests, a carbon bed as thick as the carbon bed in an actual filter, but with a much smaller cross sectional area is used. Volumetric gas flow rates through the bed are adjusted down from those of the actual filter to produce the same gas residence time in the test bed as is in the filter. In this way, the behavior of the actual filter is approximated on a smaller, more easily handled scale. Of course the test bed has a larger surface to volume ratio than the actual filter, and so will gain or lose heat more rapidly; if there are significant heat of adsorption effects, leading to a different thermal profile in the bed than in the filter, it will reduce the accuracy of the approximation. However, if the test is conducted in a relatively short time, the carbon bed is a good enough thermal insulator that heat transfer should not significantly affect the temperature profile of the bed.

Glass tubes, approximately 1 in. in diameter, were used as test beds; the tube diameter was approximately 20 times the diameter of an individual carbon particle to minimize wall effects. These tubes had coarse glass frits fixed across the tube diameter near one end to serve as a support for the activated carbon (see Figure 1). Fittings at both ends of the tube allowed it to be attached to a testing apparatus. ASC Whetlerite, provided by the COR, was used as the test carbon. A specified weight of carbon, sufficient to produce the desired bed thickness, was dropped through a 4 ft high tube into the test bed. This procedure produces a random carbon packing, avoiding channelling. The carbon-loaded bed would then be weighed, and put into the testing apparatus.

While the test apparatus was modified throughout the course of the program, the basic functions of the apparatus remained the same. Figure 2 presents a schematic of the apparatus. It consists of four major parts: the gas source, the gas pretreatment stage, the test bed, and the gas analysis stage. In most cases we used a cylinder of compressed air, nitrogen, or a mixture of nitrogen with 10,000 ppm ammonia as the gas source. Where a prolonged gas flow was required to remove preadsorbed ammonia from the carbon, a compressor was used to push lab air through the beds. Gas flow rates into the apparatus were measured by rotameters.

In the gas pretreatment stage, the gas flow was split, and various streams were bubbled through solutions to saturate them with a chemical. These solutions included water (to saturate the bed with moisture), dimethyl methyl phosphonate or DMMP (to load the bed with a strongly sorbed agent simulant), and ammonia/water (as a way of challenging the bed with ammonia). The gas streams were then recombined, prior to entering the test bed. By controlling the temperatures of the baths and the ratios of gas flow rates in the various streams, it was possible to control the concentration of additives to the gas streams. This concentration was measured by sampling the inlet gas stream and analyzing it with a gas chromatograph; in the case of a gas stream with just water as the additive, a capacitance type, relative humidity meter could be used instead. Some care had to be taken, particularly with the DMMP, to avoid liquid entrainment in the gas stream or condensation downstream of the bath. However, the apparatus was made of glass from the solution baths to the test bed (to avoid chemical adsorption/desorption over time from plastic walls, and to prevent DMMP or NH_3 reaction with metal walls), and any liquid deposition was obvious to visual inspection.

The third stage was the test bed itself. A gas tight seal between the bed and the apparatus was required. Initially this was provided by 34/45 ground glass joints. However, these introduced two problems. First, the joints had to be greased to seal properly. Often carbon fines would get into the grease, interfering with the seal. The grease also had the potential for acting as a sink for chemicals in the gas phase. And unless this grease was carefully removed before measuring the bed weight, an incorrect reading would result. The second problem was that moving the bed in and out of the apparatus required an awkward vertical displacement of the rest of the apparatus; the rigid, glass construction had to be moved as a unit. In later modifications of the equipment, the ground glass joints were replaced with flat, viton o-ring seals. These

seals eliminated the installation/removal problems with the bed; the viton o-rings provided a more certain seal, with minimal gas adsorption.

The final stage of the test apparatus was the gas analysis section. Routine analysis for the presence of significant amounts of ammonia in the gas exiting the carbon bed was accomplished by sparging the gas stream through a water bath containing phenolphthalein indicator solution. A color change in the bath indicated ammonia breakthrough. The concentration of ammonia in the water could be further quantified by using a pH probe in the solution; however, the response of the pH probe lagged 15-30 sec behind that of the indicator. Water concentration could be determined by placing a relative humidity probe into the exit stream. The concentration of other species in the gas stream could be measured by sampling the gas stream and analyzing it with a gas chromatograph.

Initial experiments were conducted with the apparatus depicted in Figure 3. Compressed air was used as the gas source. The gas stream could be humidified and/or spiked with DMMP by sparging it through the two reservoirs; it would then be combined with the bypass air stream to create the final inlet gas composition. Flow conditions and bed parameters were selected to duplicate the thickness of the C-2 canister with a 50% longer gas residence time, and are outlined in Table 3. The ammonia challenge was produced by replacing the DMMP in reservoir 2 with an ammonia/water solution. Air flow being sparged through the reservoir could be varied from 86 to 860 cm^3/min, with the rest of the gas flow being provided by bypass air; the concentration of ammonia in the gas stream could also be varied by diluting the ammonia/water solution.

The most important result of these experiments was the qualitative confirmation of the technical feasibility of this residual life measurement approach. Ammonia, in an air stream, penetrates more rapidly through a bed loaded with DMMP than through an unloaded bed; adsorbed water increases rather than decreases the ammonia breakthrough time; and it is possible to detect the penetrating ammonia with an inexpensive colorimetric reaction. Unfortunately, the results also pointed out some quantitative anomalies. In particular, for a series of experiments conducted under identical conditions, a small percentage of the breakthrough times would be significantly different. In part, these results could be attributed to gas leakage from the apparatus; in part, they were due to small differences in experimental conditions from run to run. Table 4 presents a representitive selection of these results.

Consequently, a series of modifications to the testing apparatus were undertaken in an attempt to improve breakthrough time reproducibility. First, the method of introducing the ammonia challenge gas into the inlet stream was changed from sparging the inlet stream through an ammonia/water solution to a tank of 10,000 ppm ammonia in nitrogen. This eliminated any effects of the ammonia concentration in the reservoir changing over time, or imperfect gas-liquid contacting. Second, constant temperature water was circulated through jackets around the carbon beds in an attempt to minimize thermal effects. While the carbon bed is a good insulator and will not necessarily remain at the water temperature during the course of an experiment, the water jacket provided a stable heat sink from run to run. Third, the operations of preloading a test bed with

DMMP and/or water were performed on different equipment than that used for the ammonia breakthrough testing. In this way, the experimental setups could be separately optimized for each task. And fourth, a number of different methods of detecting ammonia breakthrough were considered, including different indicator chemicals, spectrophotometric sensing of the indicator chemical color change, and nonaqueous colorimetric indicating methods, such as indicator impregnated paper or silica gel. All of these methods will indicate when the cumulative amount of ammonia breaking through the bed has reached some level. Electronic pH measurement was also considered; although slower to respond to changing ammonia concentrations than the indicators, this method has the virtue of providing a continuous measurement of the cumulative amount of ammonia in the bed effluent.

Additionally, a series of experiments were conducted to assess the sensitivity of the ammonia breakthrough time to variations in experimental conditions. The purpose of these experiments was two-fold. First, the circumstances under which a reproducible, accurate laboratory measurement of residual life could be made were evaluated. This permitted us to avoid inherently unstable experimental parameters, and, under potentially stable conditions, identified all the factors which needed to be accurately controlled to obtain reproducible results. And second, we wished to develop a realistic, accurate testing procedure for actual filters, given the practical limitations on parameters which might be measured or controlled in the field. Some of the factors considered were ammonia inlet concentration (both constant and varying as a function of time), temperature, various methods for preloading water and DMMP on the carbon bed, and pretreatment of the carbon to remove existing adsorbed ammonia. Each of these had an effect on the ammonia breakthrough time; however, the factors which seemed to produce the largest variability in the ammonia breakthrough times were the amount of water preadsorbed on the test bed and the humidity of the ammonia challenge stream. While these factors can be manipulated in the laboratory, they are uncontrolled in an actual filter. Consequently, for a field test, the amount of water adsorbed on the carbon filter and the humidity of the gas stream would have to be measured (or inferred from other data) and taken into account in evaluating the ammonia breakthrough time. Since this seems somewhat involved for an individual protection filter, it was decided to concentrate on collective protection filter conditions in the remainder of the laboratory tests. Details of these tests are presented, below.

Prior to testing, fresh ASC Whetlerite was subjected to a humid air flow for a prolonged period of time to remove preadsorbed ammonia. This treatment was continued until the ammonia concentration in the effluent had dropped to <1.5 ppm; this could require up to 7 days. It was felt that carbon pretreated in this manner was more representative of carbon in the actual filters that had been in use than was untreated carbon. The carbon was then dried in a 110 ^{o}C oven for four or more hours to remove adsorbed moisture. The carbon was weighed and stored in sealed jars until used.

For testing, the dried carbon was loaded into beds in the manner described previously. Test conditions were selected to emulate the MCPE filter and are presented in Table 5. The carbon was preloaded with water and/or DMMP under these conditions, using the apparatus depicted in

Figure 4; it was then weighed and challenged with a 7.6 L/min, 5000 ppm ammonia in N_2 gas stream. The exit stream of the bed was bubbled through approximately 225 mls of water, containing 4 drops of phenolphthalein indicator. A probe in the bath provided a continuous pH measurement.

Experimentation focused on developing a fieldable procedure for measuring the amount of water adsorbed on a test bed. Dry carbon was subjected to 7.6 L/min of 100% relative humidity (RH) air; the outlet flow temperature and RH was measured every minute. After a fixed length of time had passed, or the outlet RH had reached a fixed value, the gas flow was stopped, and the amount of water adsorbed on the bed was determined by weight. All the experimental results followed the same pattern. In the first 5 min, outlet RH would rise from 0 to approximately 30%, and outlet temperature would rise by 10-12 ^{o}C over the inlet; given the rapidly changing values, no weights were determined in this period. Further humidification produced a slower rise in outlet RH; outlet temperature would drop, but remain a few degrees warmer than the inlet stream. Over 2 hrs were required for the carbon to become fully humidified, and the outlet stream RH to reach >90%. In desorption experiments, humidified carbon was subjected to a dry air stream. In this case, the outlet RH and temperature took an initial rapid decline; after approximately 5 min the rate of RH decline slowed, and outlet temperature reached a plateau at about 10-12 ^{o}C lower than the inlet temperature.

Both adsorption and desorption water loadings versus outlet relative humidity are plotted in Figure 5; equilibrium isotherm loading levels are also plotted for comparison purposes. Despite the non-equilibrium experimental loading conditions, the data cluster around the isotherm values. Water loading as a function of outlet RH was quite reproducible at all water loading levels; and even though the amount of water loaded on the carbon was greater in the adsorption experiments than in the desorption, the difference was not great.

Figure 6 presents the ammonia breakthrough times for these beds as a function of their water loading. It has three features which should be emphasized. First, the ammonia breakthrough time has a nearly constant value of 500 sec +/- 50 sec, for water loadings between .09 -.31 gm H_2O/gm carbon. Second, for water loadings >.31 gm H_2O/gm carbon, which corresponds to nearly 100% saturation, breakthrough times increase drastically. And third, while the breakthrough time drops for water loadings between 0 -.09 gm H_2O/gm carbon, the most drastic decrease occurs at loadings between 0 - .01 gm H_2O/gm carbon. This lowest water loading value will probably not be seen in practice. For these experiments, it was achieved by drying the carbon in a 110 ^{o}C oven; even prolonged desorption of humidified carbon with a dry air flow to an outlet RH of 0%, left .02 gm H_2O/gm carbon.

The data presented in Figures 5 and 6 has been combined into a plot of ammonia breakthrough time versus outlet relative humidity, shown in Figure 7. The data is fairly well fit by the predicted breakthrough line

which has the following algebraic form:

Outlet Relative Humidity - 0-29%

A. Breakthrough time (sec)=3.275*(outlet RH)+310

Outlet Relative Humidity - 29-37%

B. Breakthrough time (sec)=16.75*(outlet RH)-82.5

Outlet Relative Humidity - 37-85%

C. Breakthrough time (sec)=540

In the field, the person running the residual filter life test would first measure the relative humidity of the air leaving the filter. If that relative humidity is less than 85%, then the test can be run. Using a table or the above equations, the person would then determine what the breakthrough time of an unloaded bed would be. If the measured breakthrough time were significantly shorter than this, it would indicate the presence of a strongly sorbed material on the carbon.

Preliminary experiments with test beds loaded with various amounts of water and DMMP confirm that this shortened breakthrough time occurs; however, the program ended before enough data could be collected to develop a quantitative correlation between bed loading and breakthrough time reduction. The results of these experiments are reported in Table 6. In all tests with DMMP loading, the material was loaded by sparging air through a bath of the pure liquid, and flowing the air through the bed. The amount loaded was determined by weight change of the bed. Presumably, the DMMP is concentrated at the front end of the bed, rather than being evenly distributed throughout. In the three experiments without adsorbed water, the carbon at the entrance to the bed actually had a wetted appearance, as if it had been soaked in liquid. In the tests with adsorbed water, the DMMP reservior was cooled to 0 ^{o}C prior to sparging with air. At this temperature, liquid DMMP has an equilibrium vapor concentration of 200 ppm, which was low enough to avoid liquid precipitation on the outside of the carbon particles. Water was loaded onto the carbon from a humidified gas stream, after DMMP loading. Under these conditions, the lowest DMMP loading of 0.05 g/g carbon showed no reduction in ammonia breakthrough time, presumably reflecting a minimal drop in the carbon residual capacity. The higher DMMP loading of 0.12 g/g carbon had a significantly shorter breakthrough time. No experiments were conducted for DMMP loading from an air stream containing very low concentrations of DMMP (<5 ppm). This would represent the most stringent test of the ammonia challenge system.

5. UNIVERSITY OF PENNSYLVANIA WORK

During this program, experimental and theoretical work on the effect of adsorbed water on the retention of water soluble and water insoluble challenge gases on ASC Whetlerite was conducted at the University of Pennsylvania. Under the direction of Professor Alan Myers, an authority

in the field of carbon adsorption, experiments were conducted by graduate students Mark Lilke and Jim Joseph. The results of these experiments, and the accompanying analysis and conclusions formed a portion of the doctoral thesis of Dr. Joseph. The relevant sections of this thesis (Chapter 4 and Appendix E) have been appended to this final report.

6. CONCLUSIONS AND RECOMMENDATIONS

Based on the work done in this Phase II program, we conclude the following:

A. Measuring the breakthrough time of a water soluble gas through a ASC Whetlerite carbon filter is a technically feasible method of determining the residual sorptive capacity of the filter, even in the presence of adsorbed moisture.

B. Ammonia is the best choice for challenge gas for this procedure. It is volatile, highly water soluble, penetrates through filters rapidly, is easily and inexpensively detected, and is relatively non-toxic. Methyl amine is an acceptable second choice; because it is less water soluble and less volatile than ammonia, adsorbed water on the carbon may not increase the breakthrough time as much as with ammonia.

C. Proper interpretation of the results of the challenge experiment will require taking various environmental factors into consideration. For example, in the Merix experiments a breakthrough time of 320 sec would indicate a bed with 100% available capacity, if there were .02 gm H_2O/gm carbon adsorbed on the bed. With .2 gm H_2O/gm carbon, the same breakthrough time would indicate a reduction in bed capacity. At a minimum, filter outlet RH and temperature should be measured and taken into account in interpreting the breakthrough time.

D. This testing procedure is best suited for collective protection filters which have a constant gas flow rate. If the equipment is modified, such that it has a minican test filter in parallel operation with the main filter, only the minican filter need be tested. This will reduce the amount of challenge gas needed, and permit use of the main filter while the test bed ammonia offgassing is vented to the environment.

E. While minican testing will indicate the reduction in filter life due to adsorbed gases, it will not indicate if the main filter has developed channeling. For the determination of filter integrity, we propose that the downstream side of the collective protection filter be covered with a porous paper, impregnated with phenolphthalein pH indicator. When dry, this paper is unreactive to acidic or basic gases. To check for filter integrity, we would first moisten this pH indicator paper, using a spray to release a specified amount of water. Then a pulse of ammonia, of low concentration and short duration, would be introduced into the air stream upstream of the filter. If the filter has integrity, the pulse of ammonia will be adsorbed on the carbon bed and advance through it over a period of several minutes, during which time the indicator paper will be dried to the point where it will not be reactive when the ammonia finally emerges. The indicator paper will than be reusable for another integrity

test at a later time. If the integrity of the filter has been compromised and there are cracks or channels through the filter, a portion of the ammonia pulse will flow through these cracks or channels and emerge rapidly at the filter outlet with a sufficiently high ammonia conentration to react with the indicator paper, which will still be moist. The ammonia will cause a color change in the detector paper in the area of a crack or channel through the filter. Examination of the porous indicator paper at the completion of the test will, therefore, enable determination of the filter integrity. To view the indicator paper in a collective protection filter, a viewing window must be added to the present units, and in some cases, lenses or mirrors may be required to observe the entire surface of the detector paper. Alternatively, the filter outer casing might be constructed of a clear plastic material.

We recommend that experimentation continue on this system. A prototype collective protection filter system, with test bed in parallel should be constructed for use in experimentation. The filters can then be loaded with water and/or a strongly sorbed agent simulant at various temperatures, and breakthrough times can be measured. These breakthrough times would then form the basis of a chart for interpreting breakthrough times measured in the field. Integrity testing of the filter could also be demonstrated.

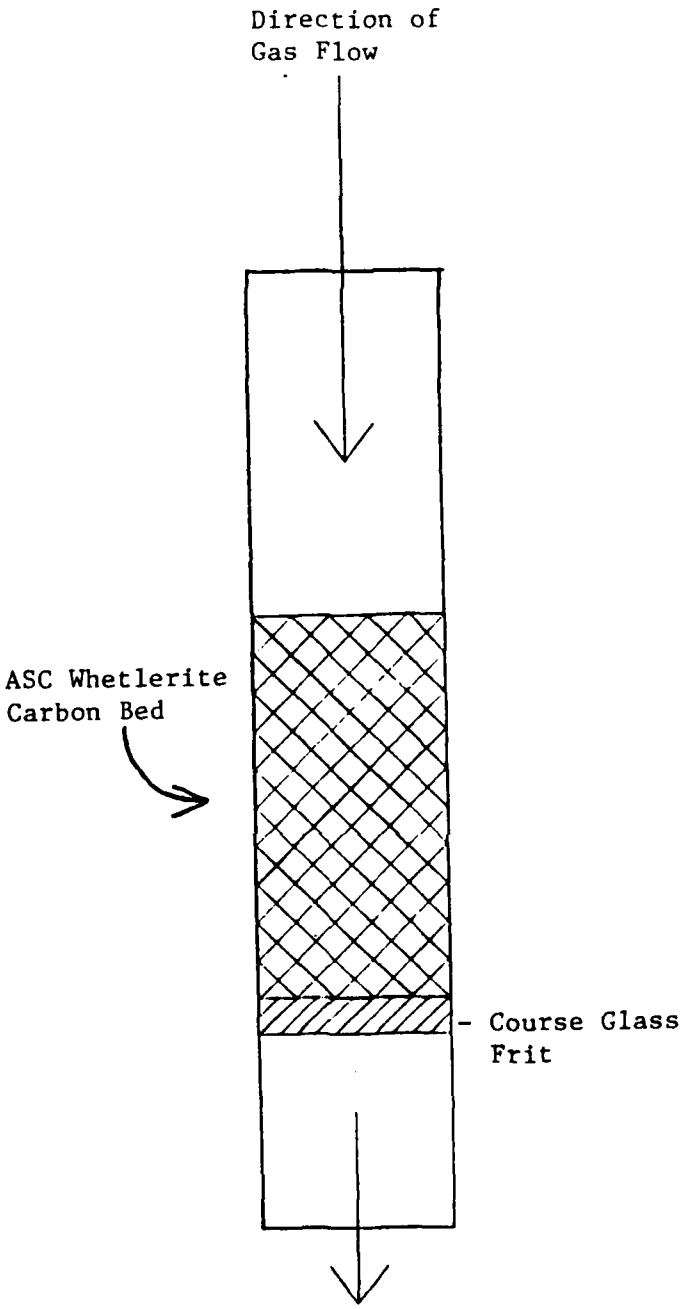


Figure 1. Schematic of Carbon Test Bed

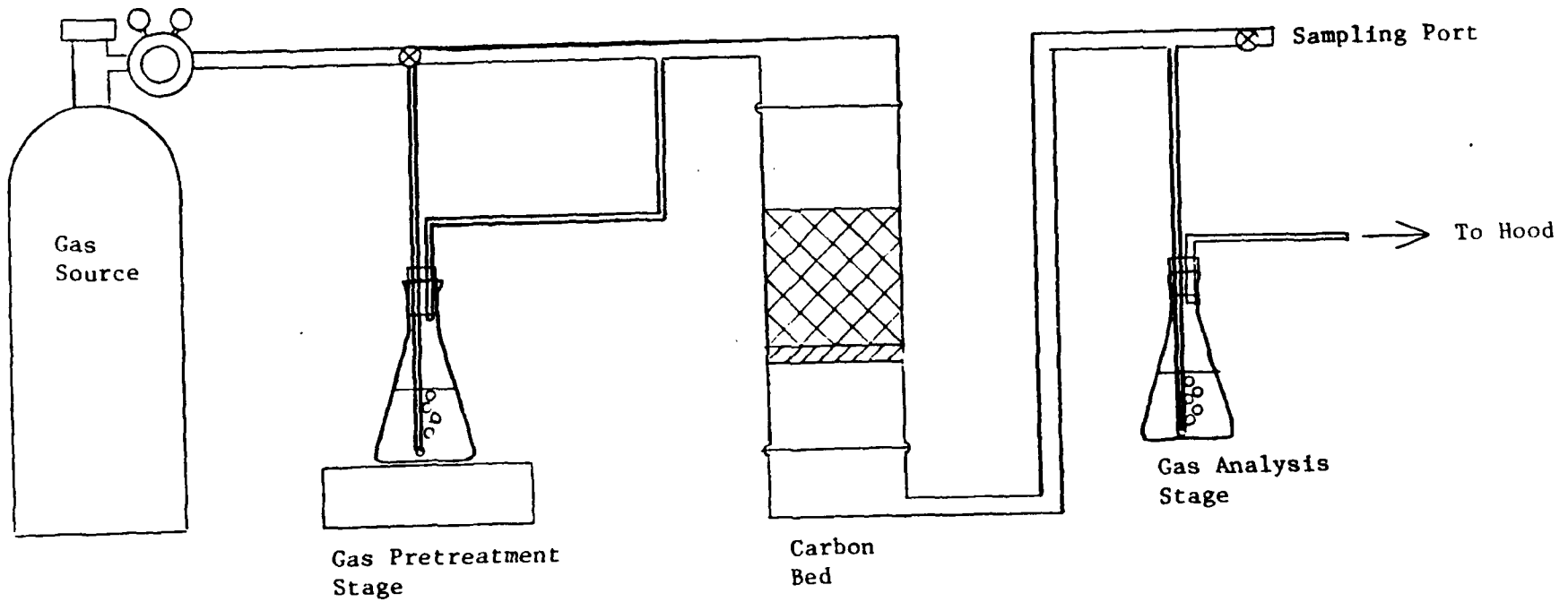


Figure 2. Schematic of Test Apparatus Basic Functions

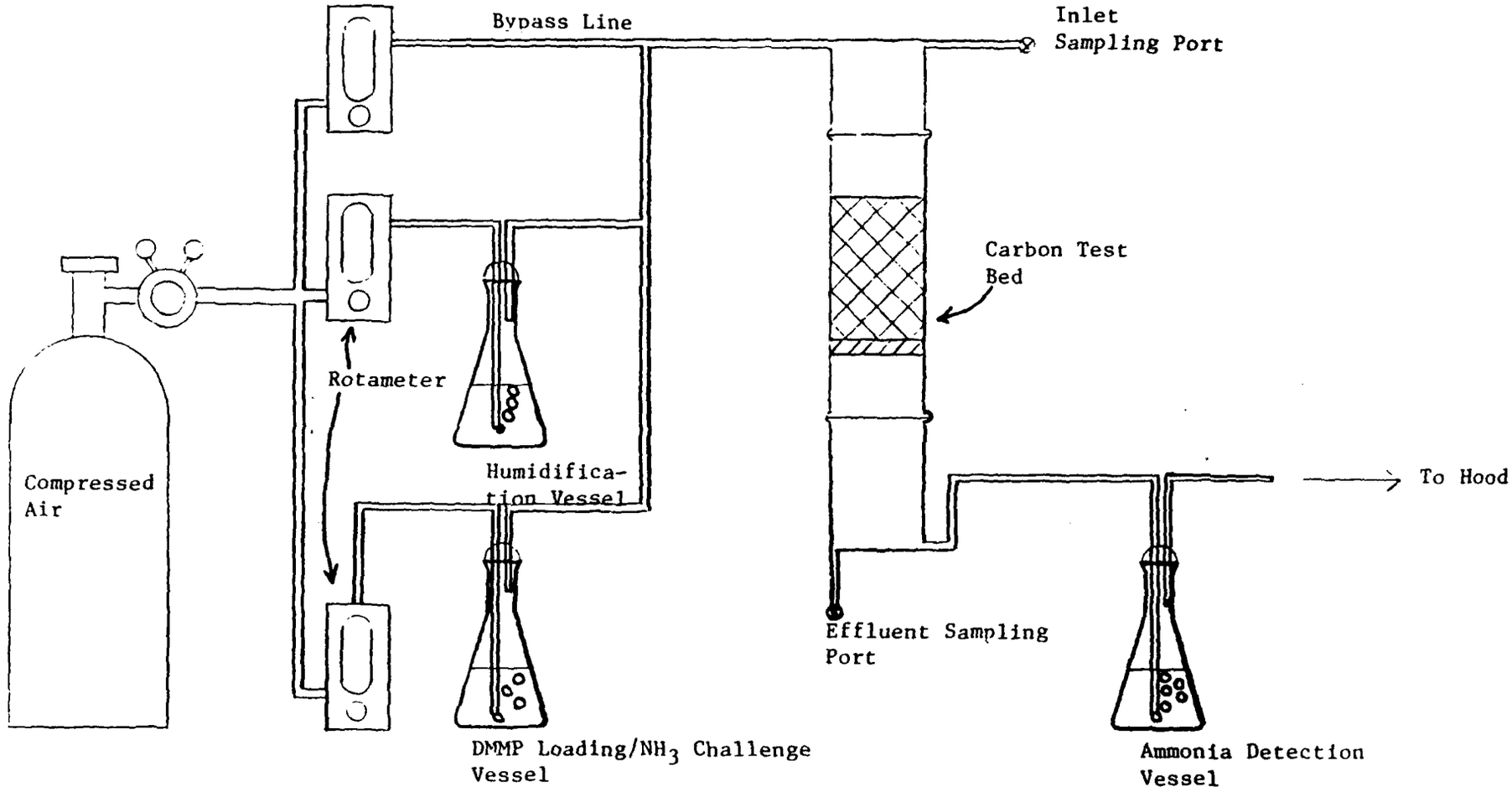


Figure 3. Schematic of First Testing Apparatus

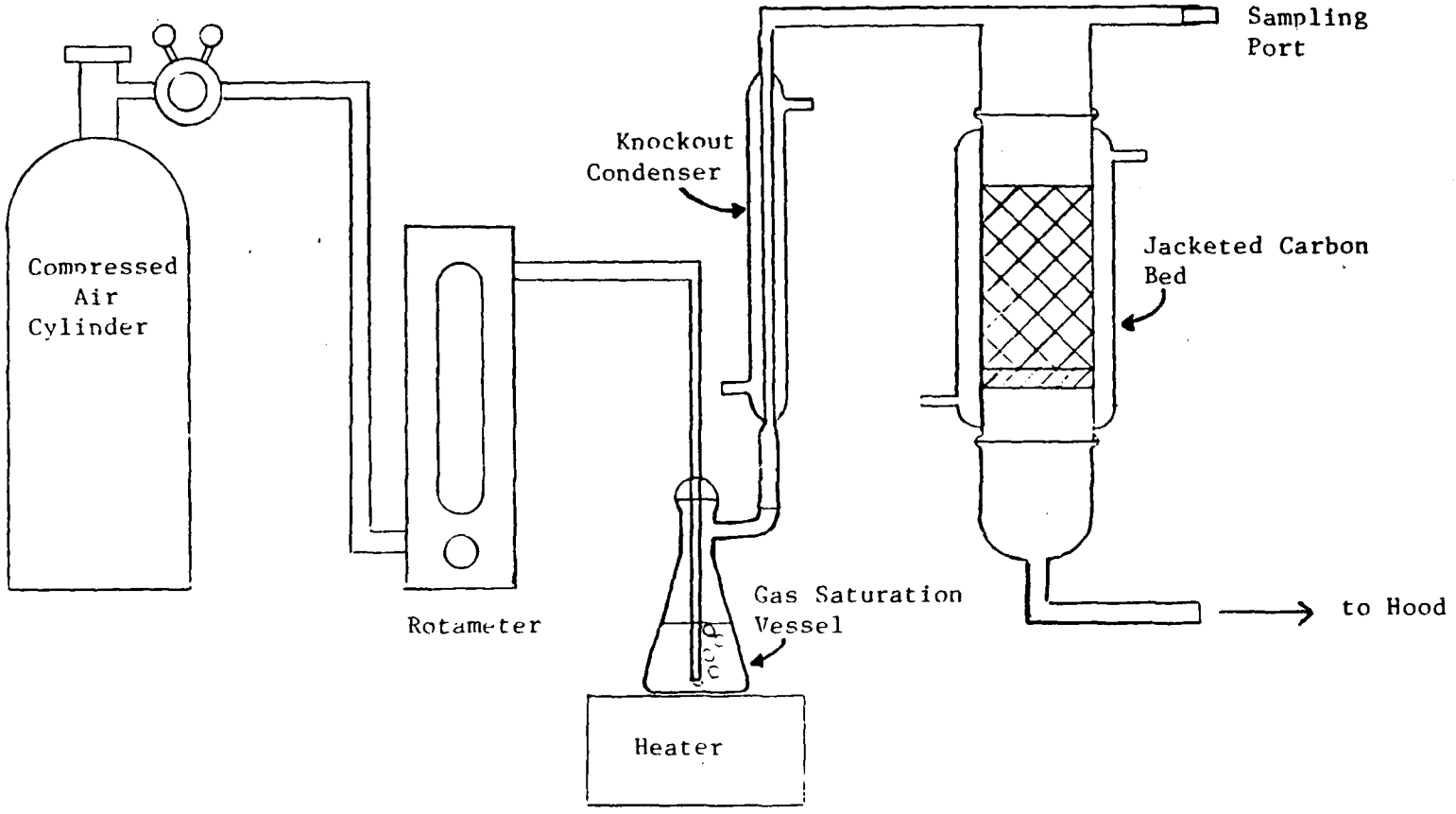


Figure 4. Carbon Bed Preloading Apparatus - Final Design

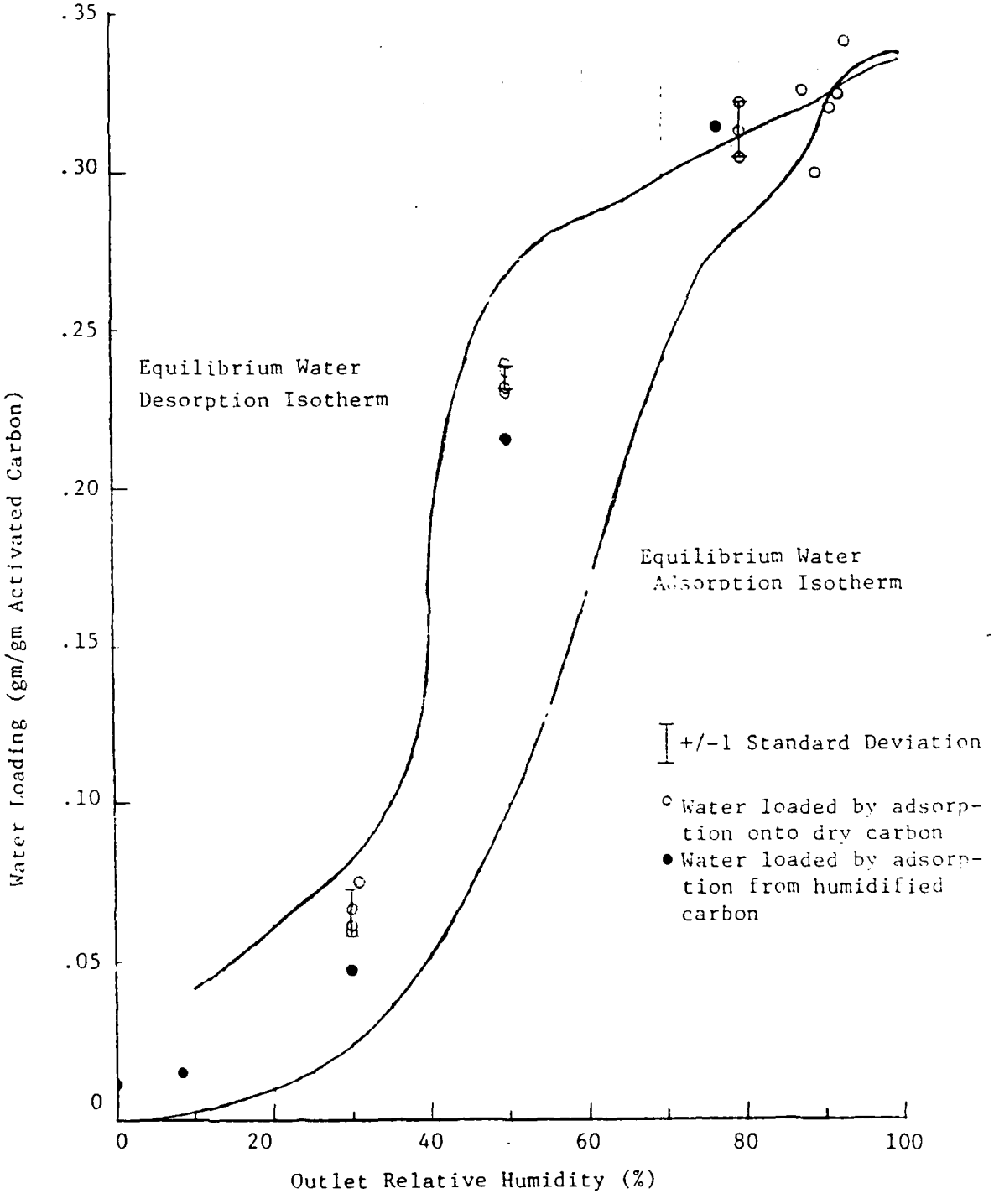


Figure 5. Water Loading onto Activated Carbon by Adsorption or Desorption from an Air Stream as a Function of Outlet Relative Humidity

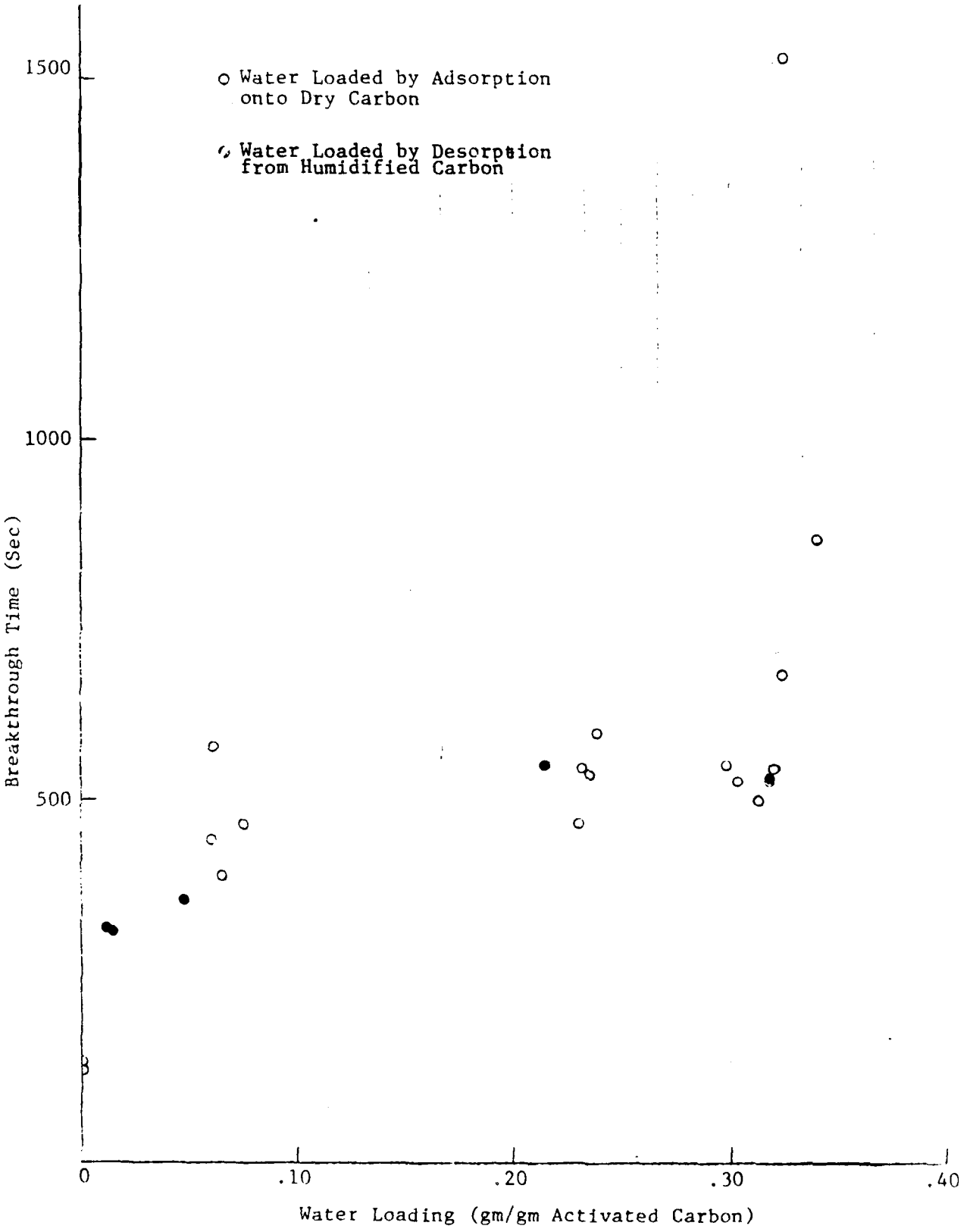


Figure 6. Effect of Water Loading on Ammonia Breakthrough Time

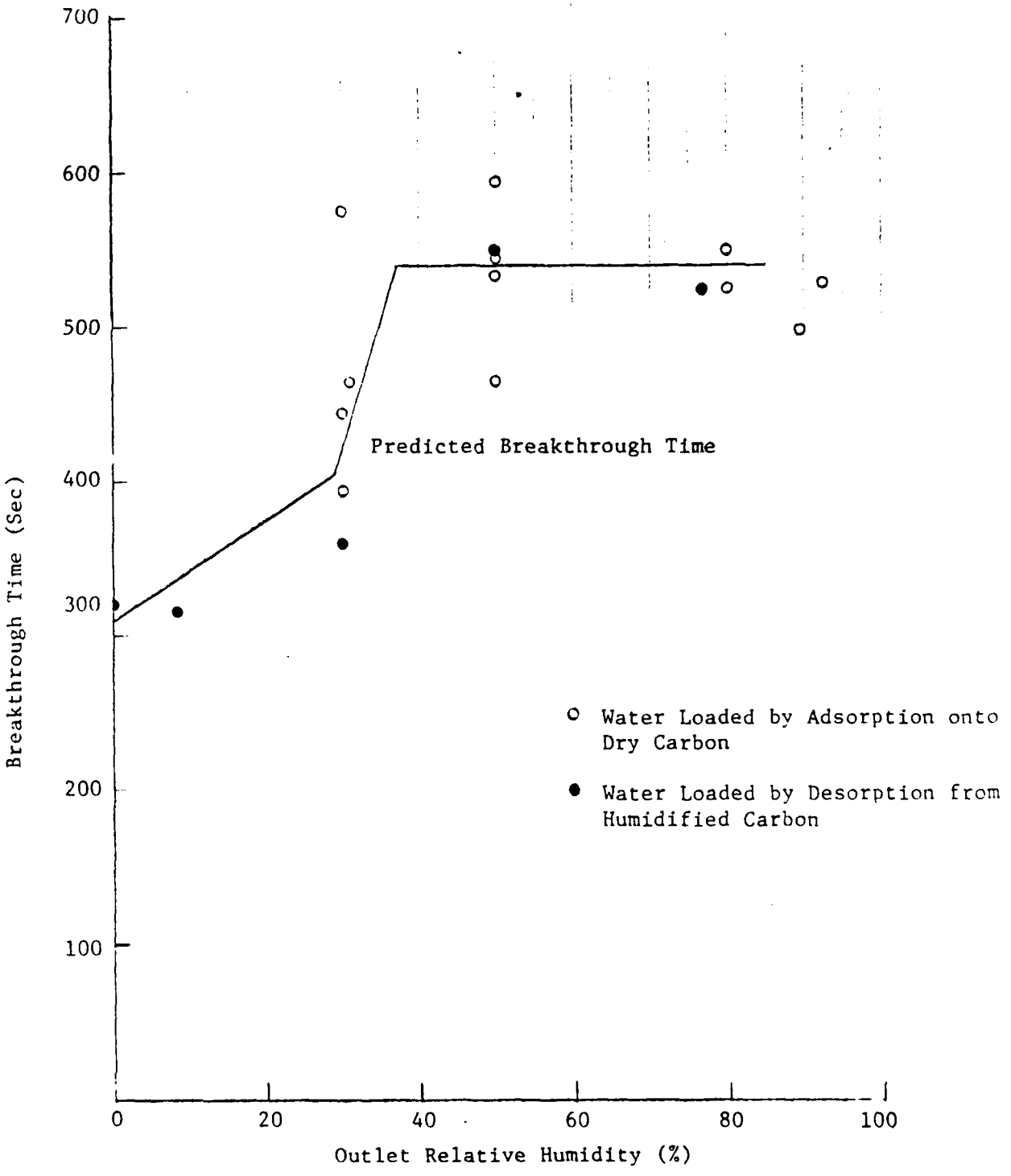


Figure 7. Relationship Between Ammonia Breakthrough Time and the Measured Outlet Relative Humidity of the Carbon Bed

Table 1. Challenge Substance Candidates

Chemical formula	Boiling Temperature	aq. solubility (ml/ml)	Comments
N_2O	-88	1.30	
C_2H_2	-84	1	TLV-2500 ppm
CF_3NO	-84		
CH_3F	-78	1.66	
C_2H_3F	-72		
C_2F_3N	-64		
C_2H_2O	-56		TLV-.5 ppm; as toxic as phosgene
CH_2F_2	-51		
C_3HF_3	-48		
$C_2H_3F_3$	-47		
C_2F_5NO	-42		
$(CF_3)_2NF$	-37		
C_2H_5F	-37		
$(C_2F_5)NF_2$	-35		
$(CH_2)_2C$	-34		
NH_3	-33	1165	TLV-25 ppm;TWA-50 ppm;IDHL=500 ppm
$(CF_3)_2O_2$	-32		peroxide
$(CF_3)_2N_2$	-31		azo compound
CF_3NO_2	-31		fluoropicrin
C_2HF	-30		
$C_2H_2F_4$	-26		
$(CH_3)_2O$	-25	37	
CHFO	-24		
CH_3C_2H	-23		
CF_3I	-22		
$(CF_3)_2S$	-22		
CH_2O	-21	300	TLV-2 ppm;TWA-3 ppm;poss. carcinogen
CF_3SO_2F	-21		
CF_3SF_5	-20		
C_2H_3Cl	-13	slightly soluble	
$CBrF_2NO$	-12		
CH_3ONO	-12		
C_3F_7NO	-12		
$(CF_3)_2NH$	-6		
CH_3NH_2	-6	959	TLV-10 ppm;IDHL=100 ppm
CH_2FCHCH_2	-3		

Table 2. Parameters for Challenge Gas Candidates

	Ammonia	Methyl ether	Formaldehyde	Methyl amine
Chemical Formula	NH_3	$(CH_3)_2O$	CH_2O	CH_3NH_2
CAS #	7664417	115106	50000	74895
Mol. weight	17.03	46.07	30.03	31.06
Melting Temp. (C)	-77.7	-141.5	-92.0	-93.5
Boiling Temp. (C)	-33.4	-24.8	-19.5	-6.3
Vapor press. at 20°C(mmHg)	6420	3820	3320	2220
Water Solub. (v/v)	1165	37	300	959
Critical Temp. (C)	132.5	126.95	134.85	156.9
Critical Press. (MPa)	11.28	5.37	6.59	7.46
Critical Vol.(cc/gmol)	72.5	170	105	154
Solubility Param.$(cal/cc)^{.5}$	14.28	8.59	11.7	11.3
Dipole Moment (Debye)	1.47	1.3	2.33	1.31
Refractive Index	1.3250	1.2984	NA	1.3491
Radius of Gyration (A)	.853	2.154	1.21	1.722
LEL (v/o)	16.0	3.4	7.0	4.9
UEL (v/o)	25.0	18.0	73.0	20.7
TVL (ppm)	25-50	NA	2	10
IDLH (ppm)	500	NA	NA	100

Table 3
Comparison of C-2 Cannister and Merix Minican Experimental Conditions

	C-2 Cannister	Merix test bed
Filter area (cm^2)	87	7.9
Filter thickness (cm)	2	2
Bed volume (cm^3)	174	15.8
Carbon weight (gm)	104	9.5
Volumetric gas flow rate (l/min)	32	1.86
gas residence time (sec)	.33	.51
Carbon bulk density (g/cm^3)	.60	.60

Table 4.
Representative Results of Ammonia Challenge of DMMP and Water Loaded Carbons

DMMP Loading (g/g Carbon) x100	Water Loading (g/g Carbon) x100	Experimental Breakthrough Time (sec)
0.00	0.00	400
0.00	0.00	382
0.74	0.00	262
1.58	0.00	193
3.68	0.00	280
6.21	0.00	168
9.79	0.00	113
0.00	2.74	401
0.00	2.84	330
0.00	3.05	420
0.00	5.89	478
0.00	6.21	432
0.00	6.53	324
0.00	6.53	408
0.00	9.37	388

Table 5.
Comparison of MCPE Filter and Merix Minican Experimental Conditions

	MCPE	Merix test bed
Filter area (cm^2)	3813	5.1
Filter thickness (cm)	5.56	5.6
Bed volume (cm^3)	21200	28.6
Carbon weight (gm)	12720	16
Volumetric gas flow rate (l/min)	5658	7.6
gas residence time (sec)	.22	.22
Carbon bulk density (g/cm^3)	.6	.56

Table 6.
Results of Ammonia Challenge of DMMP Loaded Carbons

DMMP Loading (g/g Carbon)	Water Loading (g/g Carbon)	Predicted Breakthrough Time without DMMP (sec)	Experimental Breakthrough Time With DMMP (sec)
0.05	0.107	540	555
0.12	0.156	540	390
0.21	0.000	310	235
0.39	0.000	310	95
0.69	0.000	310	5

Blank

LITERATURE CITED

1. Wheat, J.A. and Hyde, J.C., Estimation of the Residual Adsorption Capacity of Charcoal Filters, DREO Report 663, Defence Research Establishment Ottawa, Canada, September 1972, UNCLASSIFIED Report.

2. van Dongen, R.H., Non-destructive test of charcoal filters. Part III. Characteristics of the elution peaks of ethane and propane on partially spent charcoal filters of various moisture contents, TDCK 65348, Chemical laboratory TNO, Report 1974-5, UNCLASSIFIED Report.

3. Juhola, A.J., Residual Gas Life Determination Systems, ARCSL-CR-80079, Chemical Systems Laboratory, Aberdeen Proving Ground, MD, May 1981, UNCLASSIFIED Report.

4. Juhola, A.J., Probe-in-bed Technique for Determination of Residual Gas Life of Charcoal Filters, ED-CR-77021, Edgewood Arsenal, Aberdeen Proving Ground, MD, January 1977, UNCLASSIFIED Report.

5. Grain, C.F., Research and Development of a Residual Gas Life Indicator, ARCSL-CR-82036, Chemical Systems Laboratory, Aberdeen Proving Ground, MD, July 1982, UNCLASSIFIED Report.

6. Balog, P.P. and Coffman, R.C., Development of a Residual-Life Indicator for the XM48 Charcoal Filter, May 1985, UNCLASSIFIED Report.

7. Baker, J.A. and Poziomek, E.J., A Review and Perspectives on the Determination of Residual Life of Sorbents and Filters, EASP 1300-1, Edgewood Arsenal, MD, December 1972, UNCLASSIFIED Report, p.25.

8. Military Problems with Aerosols and Nonpersistent Gases, Summary Technical Report of Division 10, Vol. 1, p 144.

9. Military Problems with Aerosols and Nonpersistent Gases, Summary Technical Report of Division 10, Vol. 1, pp 157-69.

10. Juhola, A.J. and Friel, J.V., A Study of the Effectiveness of the XM-41 Filter for use with Hazardous Chemicals, USCG-D-72-77, US Coast Guard, May 1977, UNCLASSIFIED Report.

11. Handbook of Chemistry and Physics, 68th ed., ed. by R. C. Weast, CRC Press Inc., Boca Raton, FL, 1987.

12. Kirwin, Jr., C.J. and Sandmeyer, E.E., "Ethers," In Patty's Industrial Hygiene and Toxicology, 3rd rev. ed., (Vol. 2A, ed. by Clayton, G.D. and Clayton, F.E.), John Wiley & Sons, New York, NY, pp 2507, 1981.

13. Feigl, F., Spot Tests in Organic Analysis, 7th ed., pp 434-8, American Elsevier Publishing Co., Inc., New York, NY, 1966.

14. Brabec, M.J., "Aldehydes and Acetals," In Patty's Industrial Hygiene and Toxicology, 3rd rev. ed., (Vol. 2A, Ed. by Clayton, G.D. and Clayton, F.E.), John Wiley & Sons, New York, NY, p 2645, 1981.

15. Beard, R.R. and Noe, J.T., "Aliphatic and Alicyclic Amines," In Patty's Industrial Hygiene and Toxicology, 3rd rev. ed., (Vol. 2B, Ed. by Clayton, G.D. and Clayton, F.E.), John Wiley & Sons, New York, NY, p 3151-4, 1981.

16. Registry of Toxic Effects of Chemical Substances 1985-6, (Vol. 1, Ed. by Sweet, D.V.), DHHS (NIOSH) Publication No. 87-114, U.S. Government Printing Office, Washington, D.C., S/N 17-33-00431-5, p 356.

17. Bretherick, L., Handbook of Reactive Chemcial Hazards, 3rd ed., Butterworths, Boston, MA, 1985.

18. Andrews, D. M., Vapor Phase Impregnation of Active Carbons, Final Summary, Project 1B662706A095, U.S. Army Physical Research Laboratory, Edgewood Arsenal, MD, April 1970, UNCLASSIFIED Report.

GLOSSARY

CAS - Chemical Abstracts Service

DMMP - Dimethyl methyl phosphonate

IDLH - Immediately dangerous to life or health (after 30 minutes exposure)

LEL - Lower explosive limit

NA - not available

ppm - parts per million

TLV - Threshold limit value

TWA - Time weighted average (over 8 or 10 hours)

UEL - Upper explosive limit

Blank

APPENDIX

Chapter 4.

Residual Adsorptive Capacity of Gas Masks.

4.1 Introduction.

4.1.1 Motivation.

The classical gas mask familiar to soldiers and environmental protection personnel is a face-plate and a set of tubes and valves that forces inspired air through a canister of activated charcoal to remove aerosols and organic gases present in minute quantities. Modern versions contain other substances such as metal impregnants designed to react with particular toxins.

Relatively little attention has been paid to the question of determining the lifetime of a cartridge. Currently, cartridges are thrown away after they have been used for an arbitrary length of time. If the lifetime is underestimated, the cartridges are thrown away too soon; if the lifetime is overestimated, the user is placed at risk.

The work in this chapter focuses on a method for determining the residual capacity of a cartridge by measuring the time for a tracer gas to pass through the cartridge as a function of loading with a simulated toxin. Short breakthrough times are correlated with high loadings (a spent cartridge). Long breakthrough times provide assurance that the carbon is not yet exhausted.

4.1.2 Background.

Gas masks rely upon both physical adsorption and chemical reaction to remove toxic gases from the breathing supply. When gases are not adsorbed strongly onto activated carbon, removal is enhanced by reaction of the toxin with metal im-

pregnants, specifically, copper, silver and chromium (referred to as ASC whetlerite in the U.S.A.). Toxins are classified as follows [Za(45)]:

I. Physically Adsorbed Gases. Gases retained primarily by physical adsorption include mustard gas (2,2-dichlorodiethylsulfide), chloropicrin (trichloronitromethane), and many heavy organics. These gases are strongly adsorbed and can be removed effectively by adsorption alone.

II. Acid-Forming Gases. Gases such as phosgene and carbonyl chloride are hydrolyzed by moisture to form HCl and CO_2. The resulting HCl is neutralized by impregnated copper according to the reaction: $CuO + 2HCl \rightarrow H_2O + CuCl_2$. Another acid-forming gas, HCN, reacts with CuO to form cyanogen, which is then hydrolyzed.

III. Base-Forming Gases. Ammonia and other amines are retained by physical adsorption and reaction with chromium complexes. Protection against these gases is so effective that these gases are no longer used in gas warfare; however, industrial protection remains important.

IV. Oxidizable Gases. Gases such as arsine are removed by oxidation. The metal impregnants are believed to act as catalysts since they are not consumed by the removal process.

Simulants of toxic substances are used for laboratory testing. Dimethylmethylphosphonate (DMMP) closely resembles the physically adsorbed toxins. It is a large, strongly adsorbed polar molecule which blocks adsorption sites and simulates a partially exhausted cartridge. The saturation loading of DMMP on ASC whetlerite is 0.346 g/g [Kl(80)].

4.1.3 *Current Research.*

Adsorbent Improvement.

Triethylenediamine (TEDA) is used to improve the adsorptive qualities of ASC whetlerite for toxins soluble in it [US(84)], [Wo(81)]. TEDA is widely used in nuclear air cleaning to improve the adsorption of organic radioiodines and its use is being evaluated in gas mask cartridges.

Residual Adsorption Capacity.

A gas mask is a fixed bed possessing a finite adsorptive, and hence protective, capacity. However, there is no reliable method for determining the residual adsorptive capacity (RAC) of a gas mask cartridge in the field.

The goal of this work was to study adsorption as a test of RAC. A toxin or a simulant such as DMMP blocks adsorption sites and thus reduces the capacity of the adsorbent for other gases. This competitive effect can be exploited to measure the RAC of a carbon bed because the breakthrough time of an indicator gas is inversely proportional to the amount of toxin adsorbed. Either a *pulse* or a *step change* of indicator gas can be used to measure RAC.

One of the most important parameters of pulse testing is the relative humidity (RH) of the test stream [Ch(81)]. The presence of adsorbed water can "fool" pulse tests because the water blocks adsorption sites from the indicator gas. However, if the indicator gas is water-soluble it adsorbs on sites that are inaccessible to a non-water-soluble indicator, thus counteracting the effect of humidity.

The effectiveness of an RAC test depends on the method of detection. Detection can be by chemical reaction of the indicator gas, or by odor. Olfactory detection is simple but the threshold of detection varies from person to person. Despite this problem, olfactory detection is preferred to chemical detection be-

cause no equipment is required.

In this work, pulse and step changes of olfactory and non-olfactory gases were tested. The effect of humidity was studied for water-soluble and water-insoluble indicators.

4.2 Theory.

A gas mask cartridge is a specialized adsorber bed. Breakthrough of a pulse or a step change can be modelled using established theories of column dynamics. A pulse input is idealized as a Dirac delta function, while a step change is modelled as an instantaneous change in concentration. Since the delta function is the time derivative of a step change, a step-change model can be applied to both cases.

4.2.1 Column Dynamics.

Mathematical description of the dynamics of physical adsorption is one of the most difficult problems encountered in adsorption. An extensive literature describes the techniques used to solve the differential equations of column dynamics [Ya(87)]. Many theories are extensions of the original works of Rosen, Levenspiel and Bischoff [Le(63)], [Ro(51)]. Nonequilibrium models have been studied by Harwell and Hills [Ha(80)], [Hi(86)]. The effect of longitudinal dispersion has been studied extensively [Ba(66)], [Bi245(62)], [Bi257(62)], [De(56)], [Gö(85)], [Ku(65)], [La(52)], [Ra(80)], [Ra(81)]. Bashi and Gunn provide methods for estimating the intraparticle diffusivity and Peclet number from pulse inputs [Ba(77)]. Nonisothermal analysis within an adsorbent particle was presented by Brunovska [Br(78)]. Mass transfer data for use in column design has been correlated by Wakao [Wa(78)]. Others have characterized mass transfer using various empirical correlation methods and lumped parameter models [Ve(53)], [Mo(86)]. An orthogonal collocation technique applicable to many of these problems has

been presented by Caban [Ca(81)].

Adsorption in the gas mask cartridge can be modelled by two mass balances, one on the bed and one on the individual adsorbent pellet. The mass balance within a spherical pellet is:

$$D_e\left(\frac{\partial^2 C^p}{\partial r^2}+\frac{2}{r}\frac{\partial C^p}{\partial r}\right)=\frac{\partial q}{\partial t}, \tag{4.1}$$

where C^p and q are the gas phase concentration and the amount adsorbed, respectively, within the pores of the pellet as a function of the distance r from the center, and D_e is effective diffusivity. In general, for isothermal adsorption, q is a function of both the temperature T_p and the concentration inside the pore:

$$q = q(T_p, C^p) \tag{4.2}$$

Allowing for axial dispersion, the mass balance on the bed is given by:

$$-D_z\frac{\partial^2 C}{\partial z^2}+\frac{\partial uC}{\partial z}+\frac{\partial C}{\partial t}+\frac{1-\epsilon}{\epsilon}ka(C-C_R^p)=0 \tag{4.3}$$

where $\partial^2 C/\partial z^2$ is the molecular diffusion term, $\partial uC/\partial z$ is the bulk diffusion term and $\partial C/\partial t$ represents the accumulation term. This formulation assumes that the concentration is uniform radially . Constraints of continuity require that equations 4.2 and 4.3 be coupled at the surface of the pellet:

$$D_e\left(\frac{\partial C^p}{\partial r}\right)_{R_p}=k(C-C_R^p) \tag{4.4}$$

The experiment described in section 4.3 is a multiple-transition problem, with concentration wavefronts for three adsorbable components. In addition, thermal wavefronts are generated for each component. The most important simplifying assumption that can be made is to assume that the tracer gas displaces a negligible

quantity of the other pre-adsorbed components. Other assumptions are that the tracer is adsorbing in a linear region of its isotherm, and that heat dissipated is negligible and isothermal operation can be assumed. In addition, it is assumed that there is no resistance to mass transfer inside the pellet. The solution for this axially-dispersed plug flow model has been given by Levenspiel [Le(63)] and Bischoff [Bi(62)] as the solution for the breakthrough curve for linear, isothermal, trace component systems. This solution assumes constant pattern behavior, i.e. the profile assumes a shape that does not stretch or shrink as it moves through the bed. This is often a good assumption even for short beds [Ru(84)]. The outlet profile as a function of time, t, is given by

$$\frac{c}{c_o} = \frac{1}{2}\mathrm{erfc}\left\{\frac{1 - t/\bar{t}}{2\left[D_L t/(vz\bar{t})\right]^{1/2}}\right\}, \tag{4.5}$$

where c_o and c are the input and output concentrations, respectively, D_L is the *longitudinal dispersion coefficient*, z is the bed depth and v is the superficial velocity. The retention time $\bar{t}$ is defined as

$$\bar{t} = \frac{z}{v}\left\{1 + K\left(\frac{1-\epsilon}{\epsilon}\right)\right\} \tag{4.6}$$

where K is the ratio of concentrations inside and outside the adsorbent and is referred to as a dimensionless Henry's constant, and ϵ is the interparticle void fraction of the bed.

4.3 Experiment.

4.3.1 Other Work.

The retention time of methane and ethane pulses through standard M-11 gas mask cartridges has been studied by Kladnig, Weiss and Jonas [Kl(80)]. Their work correlated percent saturation of toxin with retention time for systems with no

humidity. Nelson and Harder present breakthrough curves for a large number of substances at 50% RH. No attempt was made to study the effect of adsorbed toxin or varying humidity [Ne(74)]. Chung and Sacco varied both toxin loading and relative humidity for methane and ethane, and found that the effect of adsorbed water is significant [Ch(81)].

4.3.2 This Work.

This work examines the effects of relative humidity and toxin loading, and a previously unstudied variable, the water solubility of the tracer gas. The feasibility of an olfactory detection method is evaluated.

4.3.3 Experimental Goal.

A test of residual capacity must exploit some physical change in the bed as it becomes saturated with a toxic gas. In addition, the test must not displace previously adsorbed toxic agents and allow them to be passed on to the user. The test also must not mistake adsorbed water vapor for the presence of adsorbed toxins. Two types of experiments that satisfy these criteria utilize *pulse* and *step change* inputs.

Pulse Input.

The effects of adsorption and dispersion change the retention time and alter the shape of the output pulse. The magnitude of these changes depends upon the amount of toxin adsorbed and the relative humidity.

Step Change Input.

A step-change input is modified by the same parameters that affect a pulse input. The output from a step change is sigmoidal.

4.3.4 Experimental Considerations.

Two important parameters were considered: 1. the amount of toxin adsorbed,

increases of which signal reduced capacity, and 2. humidity. Although activated carbon is not normally thought of as hydrophilic, Chung [Ch(81)] has shown that relative humidity is an important consideration in the design of a test for bed exhaustion.

The equipment was designed to measure shifts in retention time, peak broadening of pulse inputs, breakthrough curves for a constant input of a tracer gas at various loadings of a toxin simulant, all at various relative humidities.

4.3.5 Construction of Equipment.

Column. Fig. 4.1 shows the cartridge constructed to contain variable amounts of adsorbent. The body is 316 SS with a 4-inch high vacuum flange. The column is mounted vertically; the bed depth may be up to 3 inches. A retaining ring is welded inside the column to provide a support for the adsorbent. A perforated stainless steel disk, a fine mesh platinum screen, and finally a paper filter are placed on this ring. The adsorbent is then poured in and packed down. A paper filter and then a perforated stainless steel disk are placed on top of the carbon. The column is sealed by tightening eight bolts to compress the copper gasket. Ports are provided upstream and downstream for pressure measurement and concentration sampling.

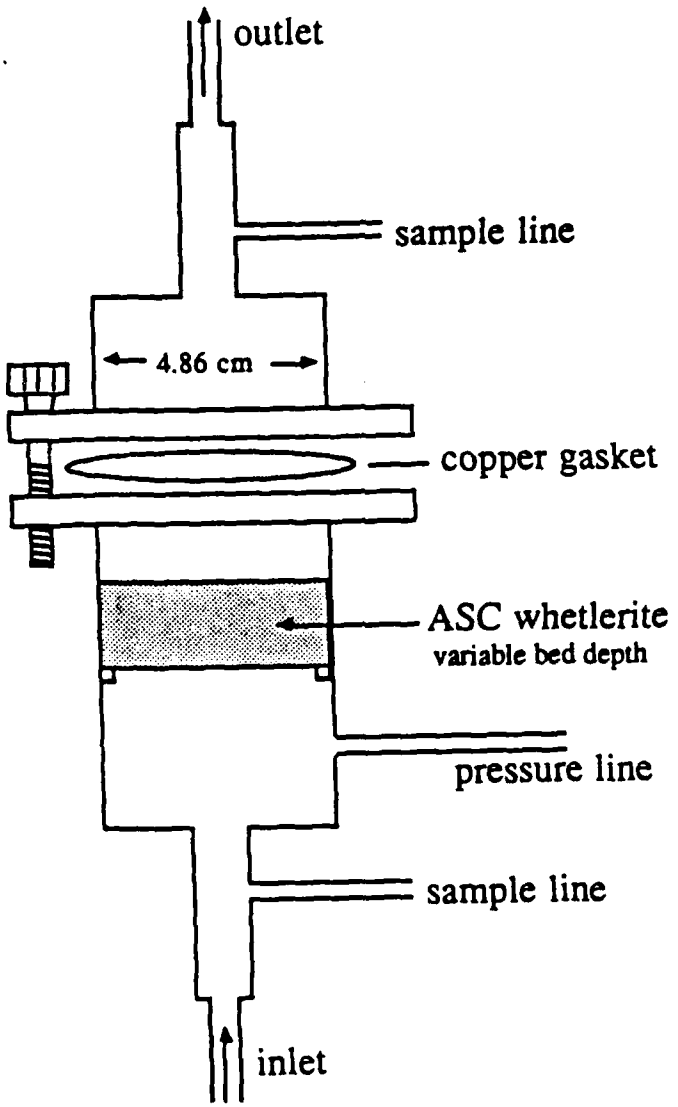


Figure 4.1. Adsorption column used as a gas mask cartridge model.

The main apparatus is shown in Fig. 4.2. The system consists of the column discussed above installed in a loop. A bypass loop is provided so that the gas can be routed around the column.

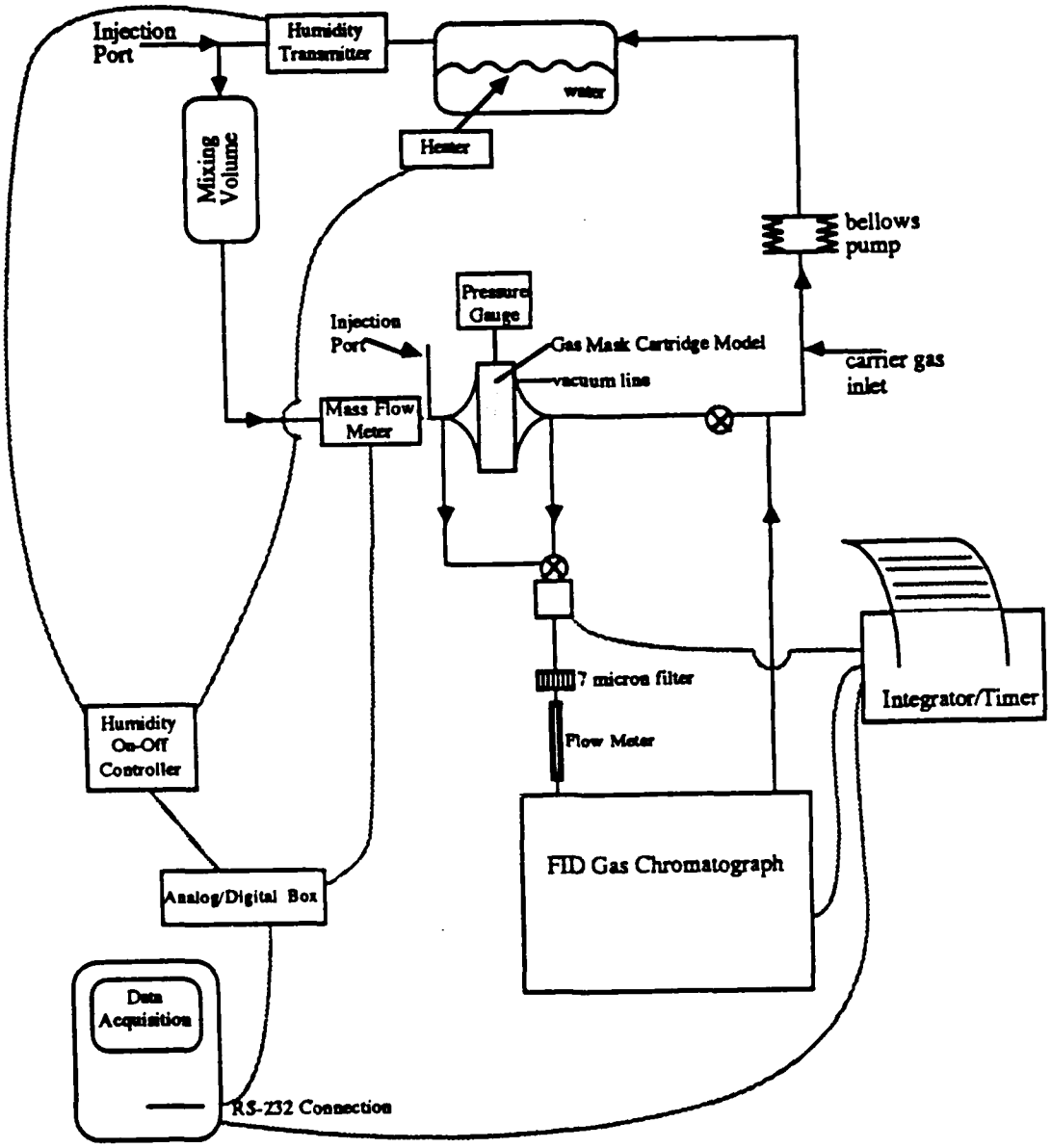


Figure 4.2. Apparatus to measure residual adsorption capacity.

Gas Chromatograph. The gas chromatograph was operated in an unconventional configuration. Ordinarily, a GC takes discrete samples; to get a continuous readout of concentration, the column was removed from the GC and the gas streams from the apparatus replace the carrier gas. Details of the gas chromatograph operation are given in Appendix D. The GC was switched between the two outlets of the column using a solenoid-operated 4-port Valco valve. The switching of this valve was controlled by programming the computing integrator, Spectra-Physics model 4270. The RS-232 output from the integrator was fed into an Apple Macintosh Plus computer.

Humidity. To simulate humid conditions the carrier gas was passed through a water reservoir. Relative humidity ($RH=P_{H_2O}/P^{sat}_{H_2O}$) was monitored at the column exit with an electronic humidity sensor; an on-off controller connected to an immersion heater maintained the reservoir at constant temperature. A stainless steel bellows pump (Metal Bellows MB21) was used to saturate the bed with water vapor. For experiments with dry gas, the flow bypassed the reservoir.

Flow Measurement. The gas flow then passed through a mass flow meter calibrated for nitrogen with a range of 0 - 20 liters/min (Omega FMA-DV-T). The mass flow meter had a mechanical totalizer and 0-5V output.

Data Acquisition. The output from the flow meter was fed into the computer by conversion to an RS-232 signal by an Omega A/D and D/A converter. The gas flow rate, concentration and relative humidity were monitored by a terminal program written in C. The program alternately polled the modem and the printer ports for incoming data, and prompted the integrator to transmit concentration data.

4.3.6 Operation of Equipment.

The operation of this equipment depended upon the type of experiment. The indicator substances were gases and liquids; some had a high vapor pressure and some a very low vapor pressure. Some were detectable only by thermal conductivity. However, the main distinction in operating procedure was pulse input versus step change input.

Pulse Input.

For a pulse input, an injection port with a gas-tight syringe was placed just upstream of the column entrance. The configuration was designed so that the injection needle delivered the pulse input well into the developed flow regime, so that the gas was immediately and completely swept into the bulk gas flow.

A typical experiment with no preadsorbed DMMP and no humidity was performed as follows. ASC whetlerite (10 g) was dried at 110°C in a helium stream for 5-8 hours. The apparatus was started in a column bypass mode and the GC was given time to attain thermal equilibrium. The carbon was then placed in the column as described previously and the column was installed in the apparatus. The gas flow was diverted through the column for a time long enough to flush atmospheric oxygen and water vapor from the system, usually about 30 minutes. Then the integrator was zeroed at the current signal level. A pulse of gas was injected as rapidly as possible using a 2 cm^3 gas-tight syringe, and the output signal was recorded on the integrator-printer and the computer.

DMMP Preloading.

DMMP was directly applied by syringe to the carbon after it had been dried. An effort was made to distribute the liquid DMMP evenly over the carbon. The carbon and DMMP mixture was then sealed in a glass vessel and shaken to help

smooth out differences in DMMP concentration in the bulk carbon. The carbon was then stored for 2-5 days to allow further equilibration.

Humidity.

The gas flow passed through the water reservoir prior to entering the column; the humidity level was adjusted to 25, 50 or 80% RH by mild heating of the water, controlled by an on-off controller. Although the outlet humidity reached the desired set point within half an hour, the carbon bed was humidified for approximately 5-6 hours because this carbon continued to adsorb water very slowly for a long period of time.

Step-Change Input.

A step change in concentration was obtained by blending a gas stream containing the indicator with the main gas stream. This gas was then diverted through the column, and breakthrough curves were obtained by monitoring the GC output. DMMP and relative humidity were handled in the same manner as above.

System Parameters.

The interparticle void fraction of the bed, ($\epsilon = 0.43$), was measured by mercury penetration. ASC whetlerite (30 cm^3) was placed in a graduated cylinder; mercury (13 cm^3) was added and compressed to force mercury in the interstices. The void fraction is $13/30 = 0.43$. The superficial velocity, v, was determined by the mass flow meter.

4.4 Results.

Olfactory Substances. Ammonia, isoamyl acetate (banana oil), menthol, vanillin, citral, n-hexyl acetate, limonene, cineole, and pinene were studied.

Non-Olfactory Substances. Nitrous oxide, propane and methanol were used. Extensive experiments were conducted with methanol and propane.

4.4.1 *Olfactory Results.*

Ammonia.

Anhydrous ammonia was used for pulse testing of RAC. On a bed of ASC whetlerite (15.11 g) presaturated with DMMP (4.752 g DMMP, percent saturation, $\theta = 0.91$), a 1 cm^3 pulse of ammonia into a stream of N_2 flowing at 3.2 liter/min either did not elute or eluted below a detectable level during a one-hour observation. This test was repeated many times, sometimes with a 2 cm^3 pulse, and no ammonia was detected in the effluent. When this test was repeated using helium as the carrier gas (which resulted in improved sensitivity for the TCD), an eluted pulse of ammonia was detected, but only about 10% of the ammonia in the input pulse passed through the bed. It is suspected that there was a significant amount of chemisorption on the metal impregnants of the whetlerite. The ability of ASC whetlerite to chemisorb ammonia has been suggested elsewhere [Za(45)], [Po(74)]. My results show that the presence of a large amount of adsorbed DMMP does not inhibit the ability of the whetlerite to chemisorb small pulses of ammonia.

To support these results, a test was made on a standard U.S. Army gas mask with a fresh M11 ASC whetlerite cartridge. A 10 cm^3 pulse of pure ammonia did not break through in a 90 minute test period.

The conclusion is that a pulse of ammonia is unsuitable to determine the residual adsorption capacity (RAC) of a gas mask cartridge. Olfactory detection is impossible if the impregnants chemisorb the pulsed ammonia, which could occur with or without pre-adsorbed DMMP.

Isoamyl Acetate.

Another potential candidate for olfactory detection was isoamyl acetate (banana oil). Isoamyl acetate is a large (MW=130.19 g/mole) organic molecule with a boiling point of 142°C. The sample used was 99% pure.

Although isoamyl acetate is strongly adsorbed on clean carbon surfaces, it was conjectured that the more strongly adsorbed DMMP would prevent the isoamyl acetate from adsorbing effectively, thus making it suitable as an indicator of the residual adsorption capacity.

When isoamyl acetate was pulsed over a bed at 80% DMMP saturation with no humidity, the eluted pulse took over an hour to appear. Since the test time should be smallest when the bed is loaded with DMMP, it was concluded that isoamyl acetate is unsuitable for use as an indicator of RAC of gas masks.

Other Olfactory Substances.

Since olfaction is the preferred method of detection, a search was conducted for other candidates, such as menthol, vanillin, citral, n-hexyl acetate, limonene, cineole, and pinene. These have low molecular weights (relative to other olfactory agents) and high vapor pressures. All exhibit low water solubility. Equal weights of these substances were mixed and used simultaneously in an experiment under the same conditions as above. The results were similar to the results with isoamyl acetate; the retention times were too long ($>$ 1 hr) to be used in a practical test to determine RAC.

4.4.2 Non-Olfactory Results.

Nitrous Oxide.

N_2O is light enough to elute in a reasonable time, non-toxic (though somewhat narcotic), and easily detected by a gas chromatograph using a thermal conductiv-

ity cell. N_2O was injected into a helium carrier gas flowing at 3.2 liter/min. Pulses of 2 cm^3 and 1 cm^3 were used over a 15 g ASC whetlerite bed at approximately 20°C. The nitrous oxide used was 99.9% pure. No humidity was used, and the DMMP preloadings used were 0, 50 and 90% of saturation.

The retention time of the nitrous oxide decreased with increased loading of DMMP on the bed as shown in Fig. 4.3. In addition, different amounts in the pulse gave the same retention time. This indicates that the adsorption isotherm is linear in the range used for these experiments. The retention times were corrected for the dead time of the system using a pulse of helium from a previous experiment when the carrier gas was nitrogen.

Another effect was a change in the shape of the eluted peaks; the width of the peaks decreased as the loading of DMMP increased as shown in Fig. 4.4.

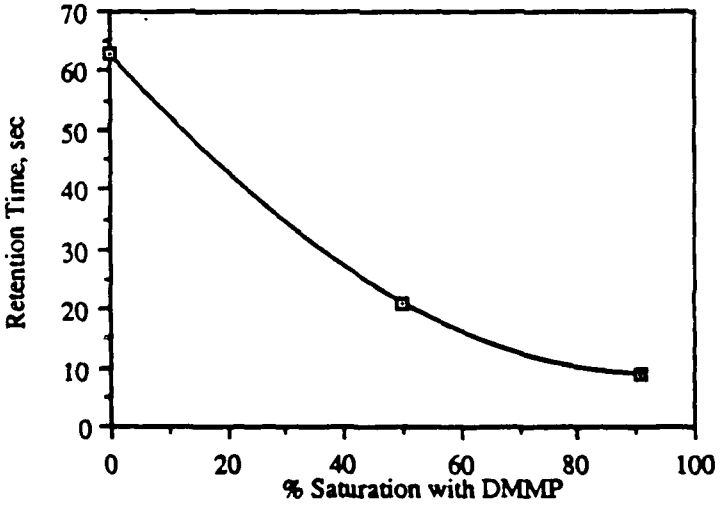


Figure 4.3. Retention time of 2 cm^3 pulses of N_2O *vs.* percent saturation of DMMP on a 15.1 g ASC whetlerite bed. Flow rate of helium carrier gas is 3.2 liters/min.

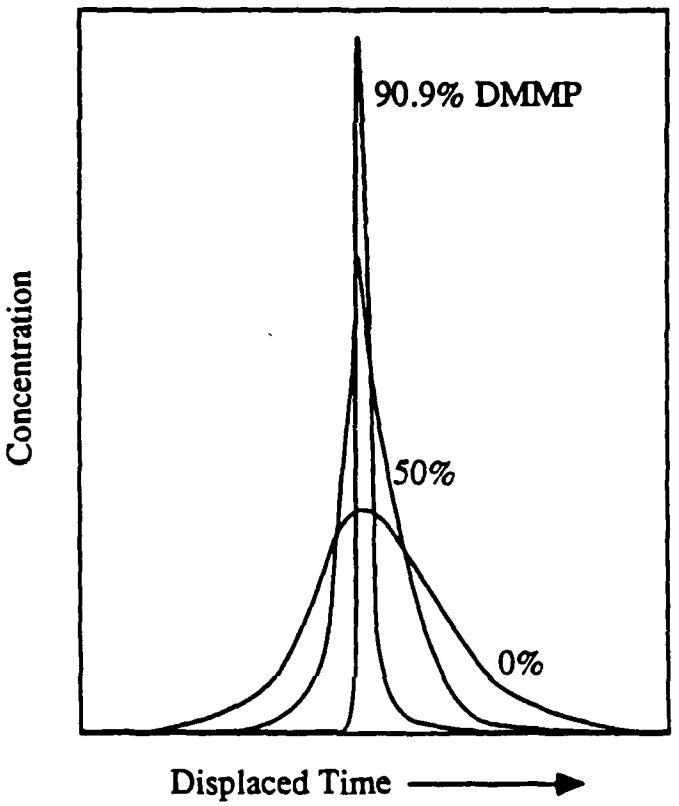


Figure 4.4. Shift of peak width with amount of preadsorbed DMMP on ASC whetlerite bed.

Although the trend of decreasing retention time with increasing loading of DMMP could provide a test of RAC, there are no suitable detection methods for N_2O in the field. In addition, I wanted the maximum retention time to be longer to improve the resolution of the experiment; i.e. differences of mir utes rather than differences of seconds. This was achieved using propane, which is more strongly adsorbed than nitrous oxide.

Propane.

Propane (instrument grade 99.9% pure) was chosen to be representative of a water-insoluble pulse gas. The amount of carbon was reduced to 10 g, and the bed depth to approximately 1 cm. The carrier gas flow rate was 6.65 liter/min and the ambient temperature varied from 18.5 to 20°C. The propane was detected using a flame ionization detector. Pulses of 1 cm^3 and 2 cm^3 were used, and, as with N_2O above, the results were independent of pulse size.

Experiments were performed at 0, 25, 50, and 80% relative humidity, with DMMP loadings of 0, 25, 50, and 80% of saturation: 16 different combinations of humidity and DMMP loading. For each combination, five to ten pulses were generated and the results were averaged.

The retention time of a pulse of propane is dramatically affected by the presence of adsorbed water and DMMP. As shown in Table 4.1, adsorbed water reduced the retention time three orders of magnitude, from 57 minutes to 0.05 minutes when nc DMMP was present. The effect of DMMP without humidity was similar. The retention times are plotted with humidity as a parameter in Fig. 4.5 and are cross-plotted with DMMP saturation as a parameter in Fig. 4.6. Also, eluted peaks were significantly broadened; this will be discussed in detail in section 4.5.

Table 4.1 Retention time in minutes of 2 cm^3 pulses of propane through 10 g ASC whetlerite bed.

Increasing DMMP loading →

↓ Increasing Humidity

	0% DMMP	25% DMMP	50% DMMP	80% DMMP
RH=0%	57	3.21	0.45	0.10
RH=25%	32	1.82	0.16	0.03
RH=50%	0.68	0.21	0.10	0.01
RH=80%	0.05	0.03	0.015	0.005

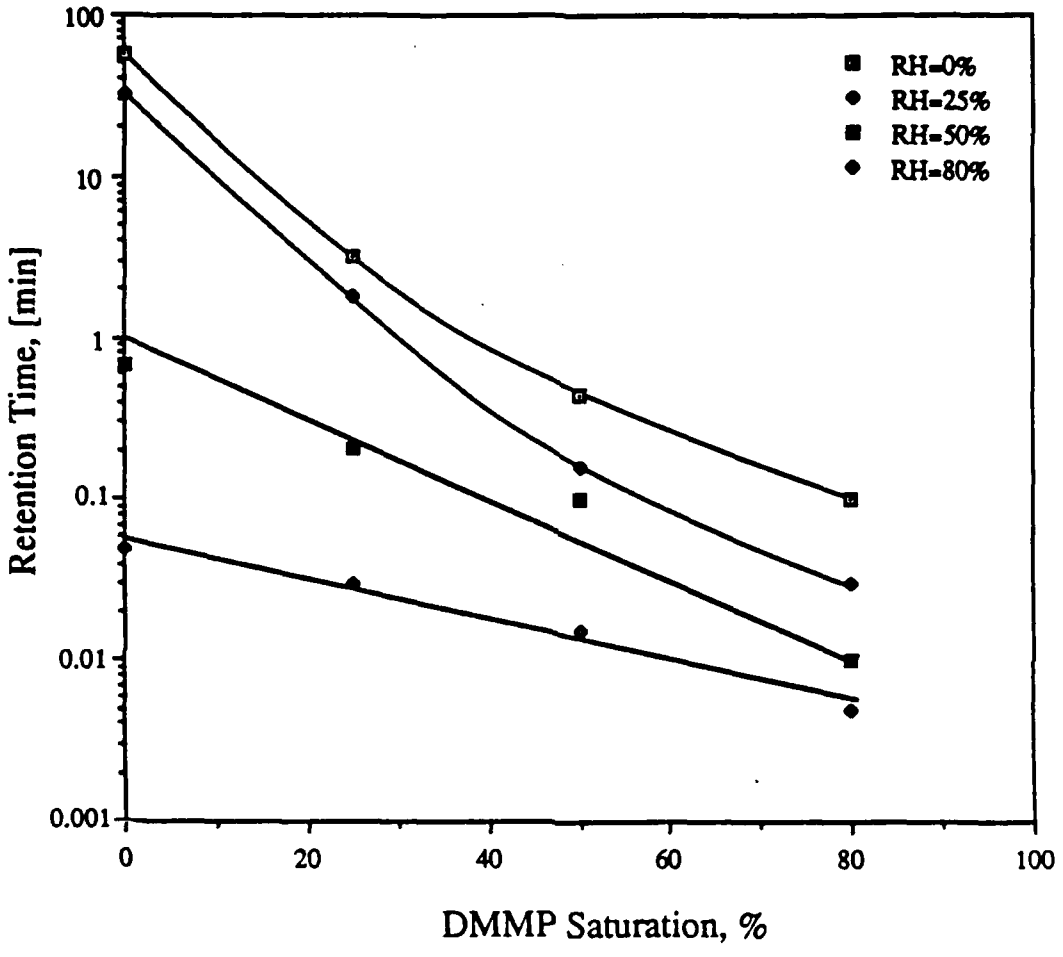


Figure 4.5. Retention time of 2 cm^3 pulses of propane through 10 g ASC whetlerite bed, with relative humidity as a parameter. Bed depth is 1 cm.

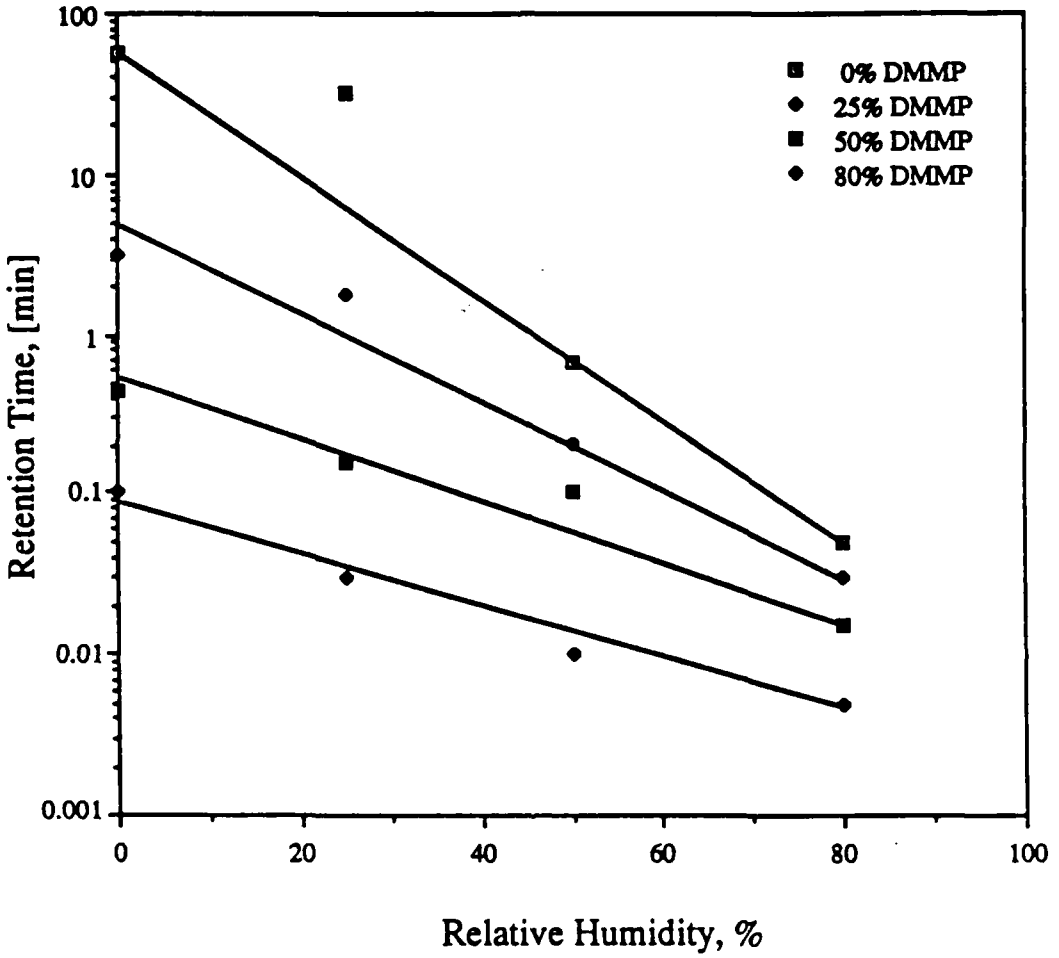


Figure 4.6. Retention time of 2 cm^3 pulses of propane through 10 g ASC whetlerite bed, with DMMP loading as a parameter. Bed depth is 1 cm.

Figs. 4.5-4.6 and Table 4.1 show that the presence of water could be mistaken for DMMP when propane is used as a pulse. Adsorbed water vapor apparently blocks adsorption sites and allows the propane to pass through the column very rapidly.

Even if the amount of water adsorbed on the bed were known, it would be difficult to use propane as an indicator of RAC because of the extent of peak broadening; very sensitive detection methods would be needed to measure the low outlet concentrations.

The retention time of a pulse of propane is affected equally by water and adsorbed DMMP, and there is significant peak broadening. Because of this, propane is unsuitable as an indicator of RAC, but its adsorption characteristics can be compared to the action of a water-soluble gas to see if its solubility will allow access to adsorption space that excludes propane.

Methanol.

Methanol was chosen as a water-soluble pulse gas because of its low molecular weight and high vapor pressure. Methanol was more difficult to work with than propane. Since methanol is a liquid, some method must be devised to introduce it as a vapor into a gas stream. One method would be to inject liquid methanol into a heated portion of the apparatus; however the time required for vaporization with this method is unknown, and therefore uncertainty would be introduced. The best procedure is to inject methanol vapor. The vapor pressure of methanol at room temperature is about 100 mm Hg, so a pulse larger than that for propane was injected. Saturated vapor (10 cm^3) was generated using a small pump to bubble nitrogen continuously through methanol in a closed loop; the vapor was withdrawn using a 10 cm^3 gas-tight syringe.

The results using pulses of methanol are presented in Table 4.2 and Figs. 4.7-

4.8. Due to strong adsorption and axial diffusion, the retention time at 0% relative humidity for 0, 25, and 50% DMMP saturation could not be measured even with the GC operating in its most sensitive mode. The data show that methanol was affected by the relative humidity, but to a smaller extent than propane. For example, at 0% DMMP the retention time of a pulse of methanol was reduced 80% when the humidity was increased from 0% to 80%; the retention time of propane was reduced almost three orders of magnitude (from 32 to 0.05 minutes) for the same conditions.

Table 4.2. Retention time in minutes of 10 cm^3 pulses of methanol saturated vapor through 10 g ASC whetlerite bed.

Increasing DMMP loading →

↓ Increasing Humidity

	0% DMMP	25% DMMP	50% DMMP	80% DMMP
RH=0%	———	———	———	260
RH=25%	56	12.2	8.4	4.86
RH=50%	35	11.7	5.1	2.21
RH=80%	12	5.11	3.04	1.98

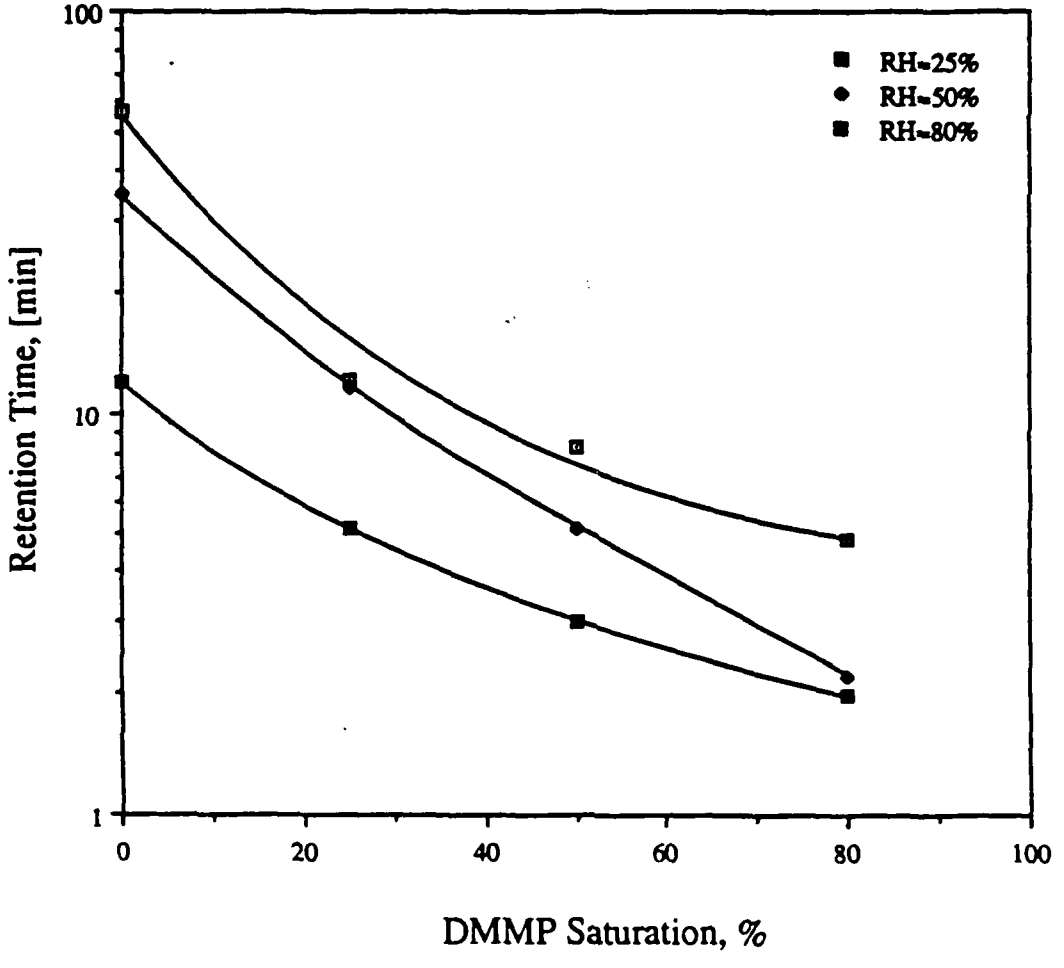


Figure 4.7. Retention time of 10 cm^3 pulses of saturated methanol vapor through 10 g ASC whetlerite bed, with relative humidity as a parameter. Bed depth is 1 cm.

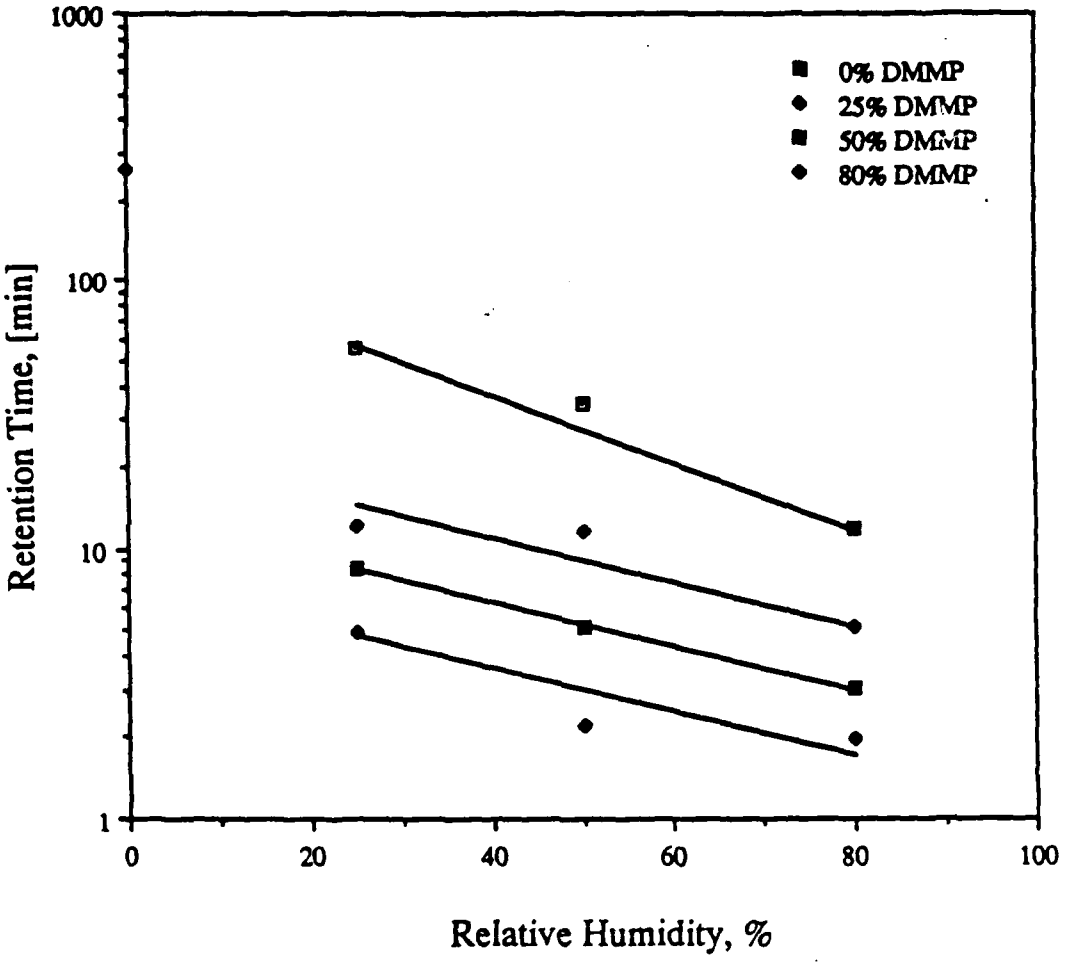


Figure 4.8. Retention time of 10 cm^3 pulses of saturated methanol vapor through 10 g ASC whetlerite bed, with DMMP loading as a parameter. Bed depth is 1 cm.

4.4.3 *Summary of Pulse Experiments.*

The results from pulse testing indicate that a water soluble pulse (methanol) is less sensitive to relative humidity than a water insoluble pulse (propane). However, an increase of relative humidity significantly reduces the retention time of methanol.

4.4.4 *Step Change Results.*

A 5000 ppm step change of methanol was introduced. The methanol stream was produced by bubbling nitrogen through liquid methanol and mixing it with the main gas flow. The outlet methanol concentration was determined by flame ionization GC analysis. The inlet methanol concentration was constant throughout the experiment. The results for four combinations of humidity and DMMP saturation are presented in Fig. 4.9. These data points were obtained by continuous monitoring of the outlet methanol concentration.

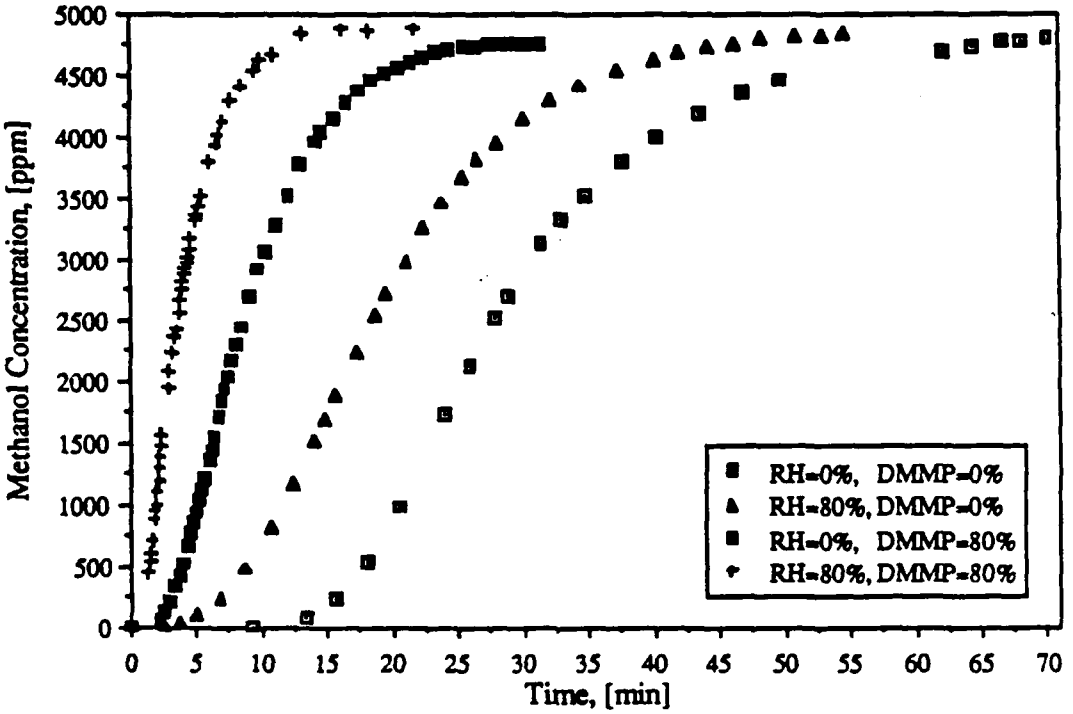


Figure 4.9. Breakthrough curves for methanol on a 10 g ASC whetlerite bed (depth=1 cm) at 19.0°C. Flow rate of nitrogen carrier gas is 6.7 liter/min.

These results show that the retention time for a large step change of methanol was reduced by the presence of adsorbed water, but to a lesser extent than for pulse injections used earlier.

A step change could be used to determine the RAC by timing the breakthrough of a pre-set threshold concentration. For example, with this data, if 4000 ppm were chosen as the threshold concentration, then a clean bed with no humidity and no DMMP would give a time-to-threshold of 40 minutes. If the same bed were then equilibrated at 80% RH, this time would be reduced to 28 minutes,

which is only a 30% reduction. The breakthrough curves with 80% DMMP intersect the 4000 ppm mark at 14 and 6.5 minutes for 0% and 80% RH respectively. If the goal is to detect 80% DMMP saturation, then the bed should be declared exhausted when the retention time is 14 minutes or less. This is a conservative estimate.

Previous work using a pulse input indicated that the effect of humidity was so strong that a mask equilibrated at 80% humidity could be mistaken for one saturated with DMMP. This is not the case for the step changes of methanol as shown in Fig. 4.9. For trace pulses, the humidity effect swamped the DMMP effect sufficiently to doubt the effectiveness of a pulse as an indicator of RAC. Although a step change works in the laboratory, there remains the practical problem of generating a step change of indicator gas in the field. These experiments require a steady gas concentration. Further investigation should focus on the use of a square wave input, which is a compromise between a pulse and a step change.

Interaction of Water Vapor and DMMP .

The adsorbent was prepared for these experiments by first loading with DMMP and then equilibrating with water vapor. It was possible and likely that the carrier gas sweeps away some of the DMMP during the course of an experiment and therefore reduces the actual loading of DMMP. To check the magnitude of this effect, the ASC whetlerite was weighed at the end of an experiment. Pulse gases were allowed to pass completely through the column, as verified by the gas chromatograph. Then, the humidity was lowered to zero and the water on the column was desorbed, after which the carbon was removed from the column and weighed. The weight was equal to the initial weight of the carbon plus the weight of DMMP added within about 5%, suggesting that water vapor does not significantly displace adsorbed DMMP.

The carbon beds were humidified slowly enough not to overshoot the desired humidity level, since hysteresis is common with water adsorption. Fig. 4.10 below shows a breakthrough curve for an inlet stream of 30% RH. The outlet reaches 2/3 of the inlet level within 10 minutes, but the approach to 30% RH was much slower. If the beds were not equilibrated at the desired humidity, a trend of decreasing retention time of a pulse was observed. However, when the beds were humidified for 4 or more hours, steady measurements were obtained.

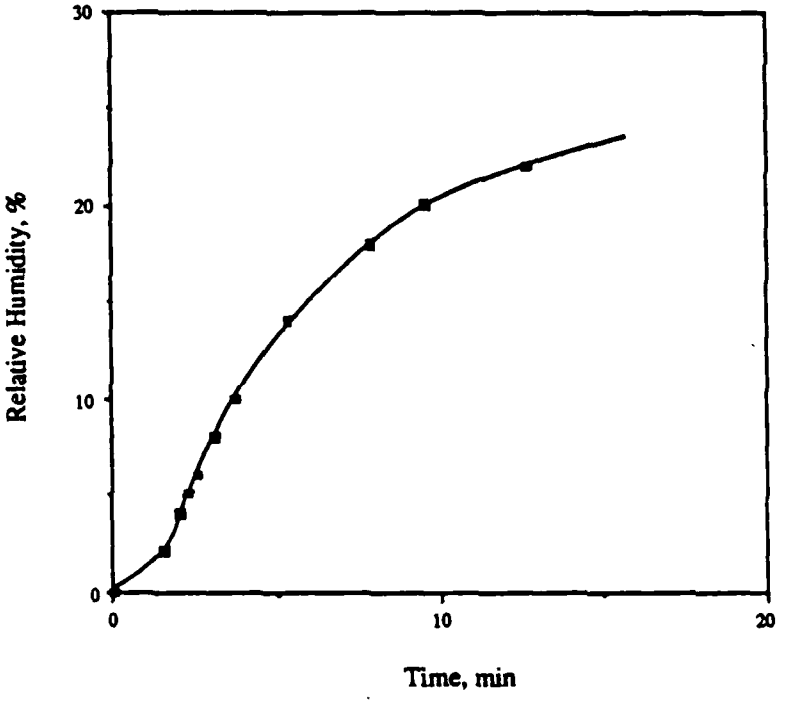


Figure 4.10. Breakthrough curve for 30% relative humidity in nitrogen at 20°C on 10 g ASC whetlerite bed.

The presence of pre-adsorbed DMMP reduced the amount of water vapor adsorbed on the beds. As shown in Fig. 4.11 below, the amount of water adsorbed was reduced from about 0.33 g/g to about 0.15 g/g as the loading of DMMP

increased from 0 to 80% of saturation. This is consistent with the high adsorptive strength of DMMP. These figures were determined by weight at the end of an experiment.

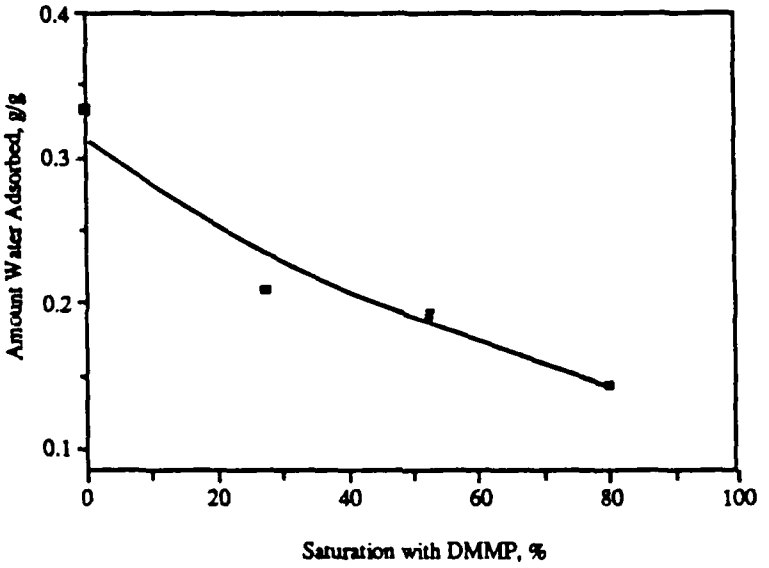


Figure 4.11. Reduction in amount of water vapor adsorbed as loading of DMMP increases.

A check was made to ensure that methanol adsorption displaced a negligible amount of pre-adsorbed DMMP. At the end of an experiment the methanol was desorbed and the carbon was removed and weighed. Its weight was equal to the total of the weight of carbon and the DMMP added, indicating that a negligible amount of DMMP was displaced by the adsorbing methanol.

4.5 Theory and Discussion.

Experimental results presented in the previous section indicate that a step-change input is more suitable as a test of RAC. The goal of this modelling is to be able to predict breakthrough curves for a step change of gas whose adsorptive characteristics on clean ASC whetlerite are known. An important unknown parameter in Eqn. (4.5) and (4.6) is the longitudinal dispersion coefficient. In section 4.5.1, the pulse experiments are used to determine the change in D_L with both DMMP preloading and relative humidity. In section 4.5.2, the methanol step-change experiments are modelled.

4.5.1 Pulse Experiments.

The response to a pulse input begins well before the peak concentration is reached and rises very slowly to the maximum. In gas chromatography [Et(67)] [Me(84)], this is called a *leading front.* This behavior is caused by axial diffusion and unfavorable adsorption characteristics. The adsorption of propane or methanol on activated carbon is termed *favorable* because the incremental amount adsorbed decreases with increasing pressure, i.e., dn/dp decreases with pressure. In a column, this causes high concentrations to travel faster than low concentrations, so that the front of a peak is *self-sharpening.* The leading front must therefore be caused by axial dispersion.

After the concentration peaks, the response tails off even more slowly than it rises. The same effect that causes a self-sharpening front causes a tailing peak. Low concentrations travel slower than high concentrations so the tail has a tendency to spread out. Axial dispersion contributes to the length of the tail.

It was observed experimentally that the tail was always longer than the front. The front is broadened by axial dispersion and sharpened by favorable adsorption.

while the tail is broadened by both axial dispersion and the favorable adsorptive characteristics. In other words, both dispersion and adsorption contribute to a broad tail, while these effects compete to determine the shape of the front

Strongly adsorbed substances with long retention times exhibit significant peak broadening due to axial diffusion and peak tailing. The phenomenon of peak broadening would make an indicator test very difficult to perform in the field; fortunately, the sharpest peaks occur when adsorption is made weaker by humidity or the presence of adsorbed DMMP.

The amount of peak broadening can be characterized by defining a parameter β such that

$$\beta = \frac{\text{peak height}}{\text{peak width}}$$

where the peak width is measured at the half-height as shown in Fig. 4.12.

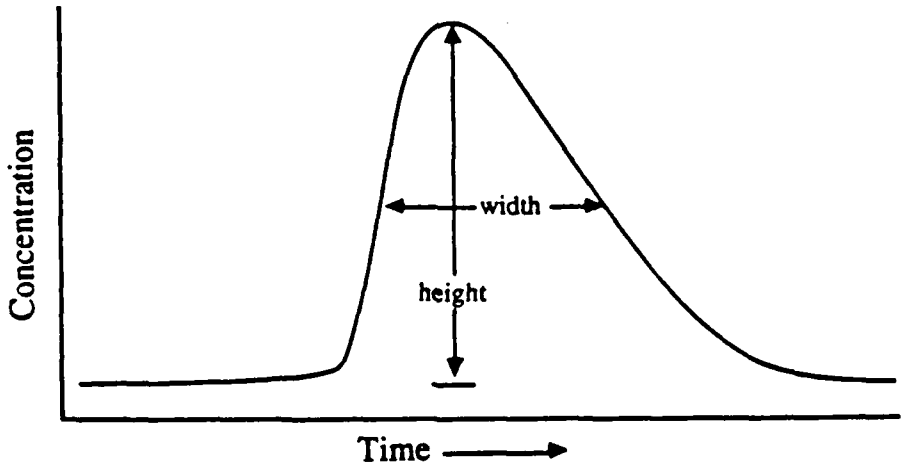


Figure 4.12. Measurements used to characterize peak broadening.

Small values of β indicate a broad peak that can be detected only by a gas

chromatograph operating in its most sensitive range. The experimental values of β for propane are shown in Table 4.3 below.

Table 4.3. Experimental values of β for 2 cm^3 pulses of propane through 10 g ASC whetlerite bed.

Increasing Humidity ↓ / Increasing DMMP loading →	0% DMMP	25% DMMP	50% DMMP	80% DMMP
RH=0%	0.075	6.2	110	3030
RH=25%	0.13	15	1100	14000
RH=50%	36	470	2500	26000
RH=80%	7500	14000	27000	36000

Table 4.4. Experimental values of β for 10 cm^3 pulses of methanol vapor through 10 g ASC whetlerite bed.

Increasing Humidity ↓ / Increasing DMMP loading →	0% DMMP	25% DMMP	50% DMMP	80% DMMP
RH=0%	——	——	——	0.22
RH=25%	——	9.1	17	59
RH=50%	1.0	11	37	76
RH=80%	5.9	47	80	735

The dispersion coefficient is calculated by assuming a value of D_L, determining the shape of the response curve (β), and comparing it to experimental data; details of this calculation are given in Appendix E. The results of these calculations are shown in Figs. 4.13-4.14 for propane and Figs. 4.15-4.16 for methanol. Methanol shows a smaller variation in the dispersion coefficient than propane, while the dispersion coefficient decreases with increasing loading of DMMP or water for both gases. This is due to a change in the time lag associated with heat transfer, molecular diffusion or other physical changes [Gõ(86)]. The dispersion coefficient for methanol is less affected than that for propane because methanol is soluble in both water and DMMP; propane is blocked from some pores because it is insoluble in these substances.

The important conclusion from this modelling is this: The longitudinal dispersion coefficient for methanol is less affected by DMMP and water than is D_L for propane.

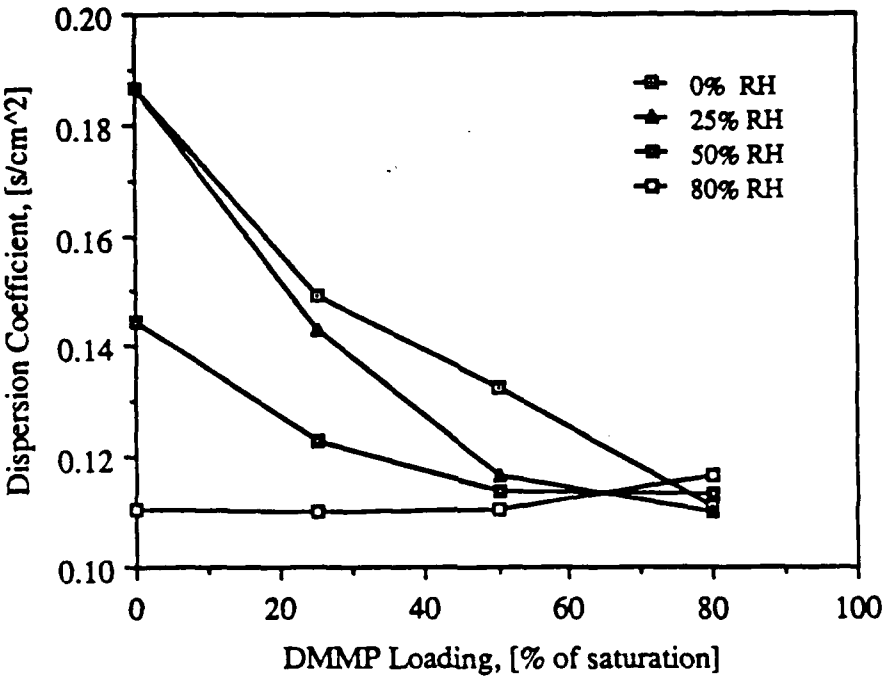


Figure 4.13. Longitudinal dispersion coefficients for propane on ASC whetlerite bed with relative humidity as a parameter.

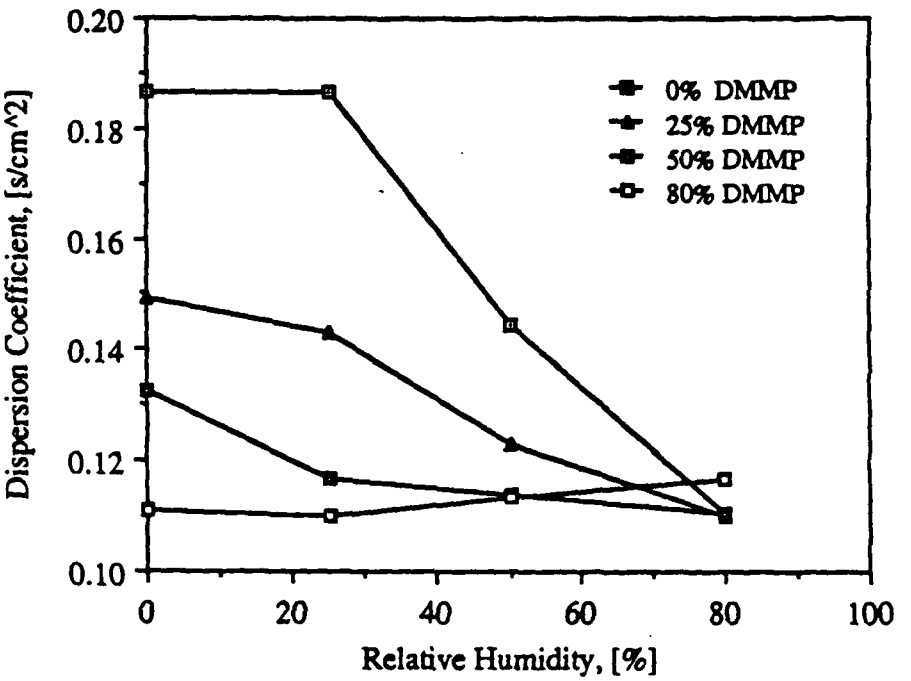
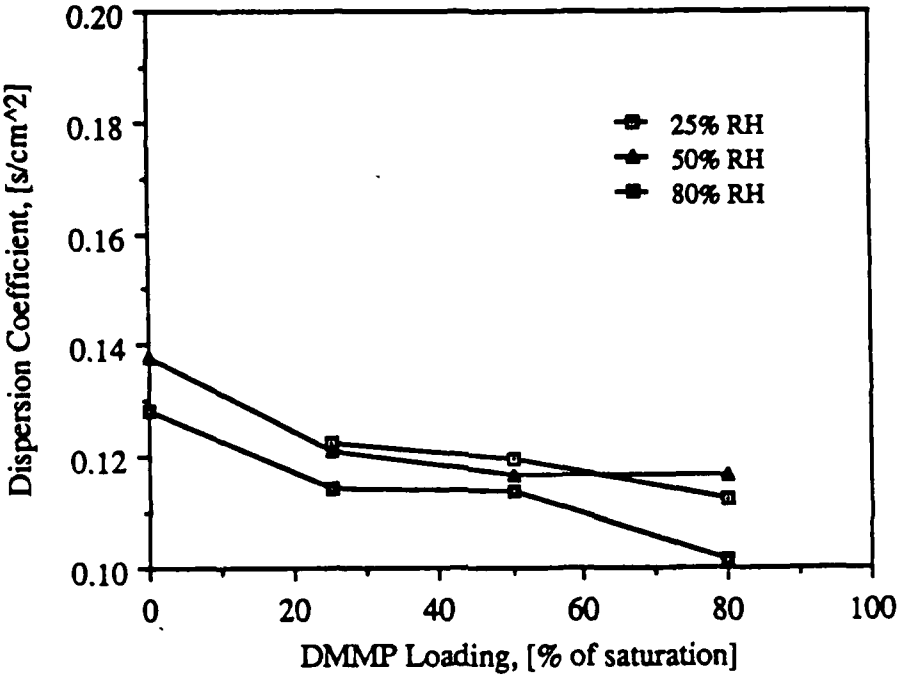


Figure 4.14. Longitudinal dispersion coefficients for propane on ASC whetlerite bed with DMMP loading as a parameter.



F gure 4.15. Longitudinal dispersion coefficients for methanol on ASC whetlerite bed with relative humidity as a parameter.

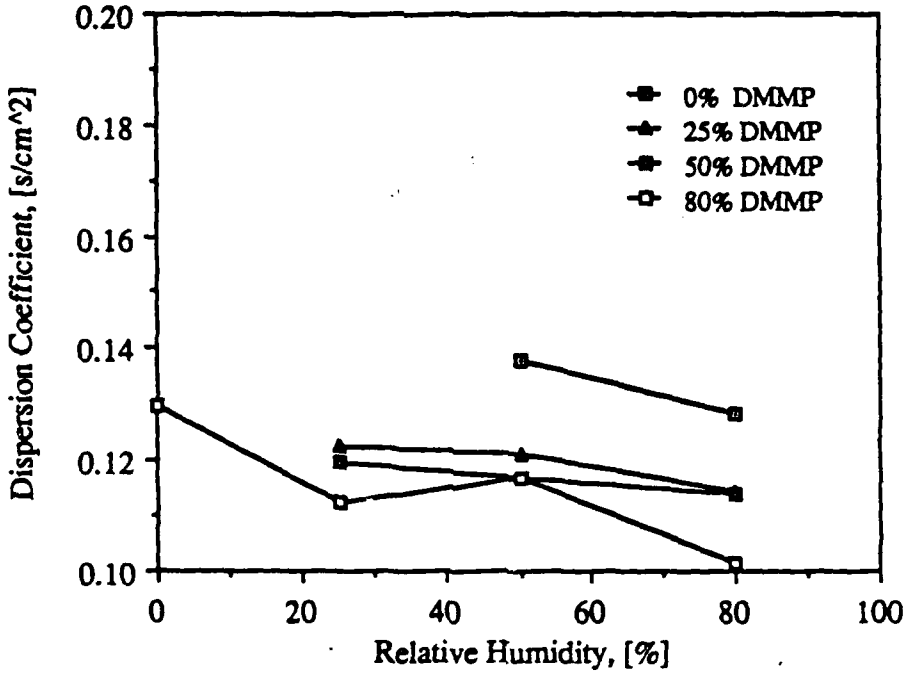


Figure 4.16. Longitudinal dispersion coefficients for methanol on ASC whetlerite bed with DMMP loading as a parameter.

4.5.2 Step Change Experiments.

The methanol breakthrough curves in Fig. 4.9 were modelled using the result of Levenspiel and Bischoff, Eqns. (4.5-4.6). Details of the calculations are given in Appendix E. The output profile is a function of D_L and K. The breakthrough curve for clean ASC whetlerite (no DMMP or humidity) was fit with Eqn. (4.5) by a dimensionless Henry's constant of 8000, and a longitudinal dispersion coefficient of 0.4 sec/cm^2.

The results from methanol pulse testing (section 4.5.1) indicate that the dispersion coefficient does not change dramatically with changes in DMMP or water loading; the value of D_L was held constant, and IAST (discussed in Chapter 3) was used to predict the Henry's constant for methanol at 80% DMMP loading and 80% relative humidity, and each condition separately. Isotherms from the literature were used for DMMP and water loading on ASC whetlerite. The DMMP isotherm used was taken from a graph given by Cheselske [Ch(68)]; the water isotherm was taken from a graph by Chung [Ch(81)]. A methanol isotherm was measured (see Chapter 2) on BPL activated carbon to serve as the model for the effect of DMMP and water on the Henry's constant of methanol. If IAST predicted a 50% reduction in the Henry's constant on BPL carbon, it was assumed that the Henry's constant showed a similar decrease on ASC whetlerite. Given the approximate nature of the pure component data for water and DMMP (taken from graphs), and that methanol adsorption was measured on BPL carbon rather than ASC whetlerite (discussed in Chapter 2), the predictions of K are estimates at best. The values calculated were:

Table 4.5. *Values of K calculated for different combinations of relative humidity and DMMP saturation.*

RH, %	DMMP, %	K
80	0	3130
0	80	1520
80	80	1480

These calculations were performed by specifying the partial pressure of water and the amount of DMMP adsorbed. Previous experiments have shown that DMMP is negligibly displaced by adsorbing water, so the amount of adsorbed DMMP was assumed invariant. These values of K were used to predict the response to a step change of methanol when DMMP and water were present (experimental data shown in Fig. 4.9); the result of the prediction is given in Fig. 4.17. Curves with humidity and DMMP are *predictions*, while the curve without DMMP or humidity is a *fit*.

Although the predictions are crude, trends of the variation of retention time with loading of DMMP and water are reproduced. Some of the error is due to uncertainty in the equilibrium data for water and DMMP.

These results show the effect of water solubility of methanol. A physical adsorption theory such as IAST does not account for *absorption* phenomena which may be occurring in this system. For example, the breakthrough curve predicted for a relative humidity of 80% with no DMMP shows much more inhibition of adsorption than the experimental curve. If methanol absorbs in water in the pores,

this would give a longer retention time than that predicted by a purely competitive model; adsorption-desorption as well as absorption-stripping processes may be occurring.

Conclusions of Step-Change Modelling.

1.) Qualitative trends of breakthrough times in the presence of DMMP and water are reproduced, but this model could not be used to predict accurately the breakthrough time for varying conditions of DMMP loading and relative humidity.

2.) Reliable pure-component isotherms on ASC whetlerite are required for DMMP, water, and methanol; the isotherms used for this modelling were approximate.

3.) The effect of absorption could cause the observed deviation of theory from experiment.

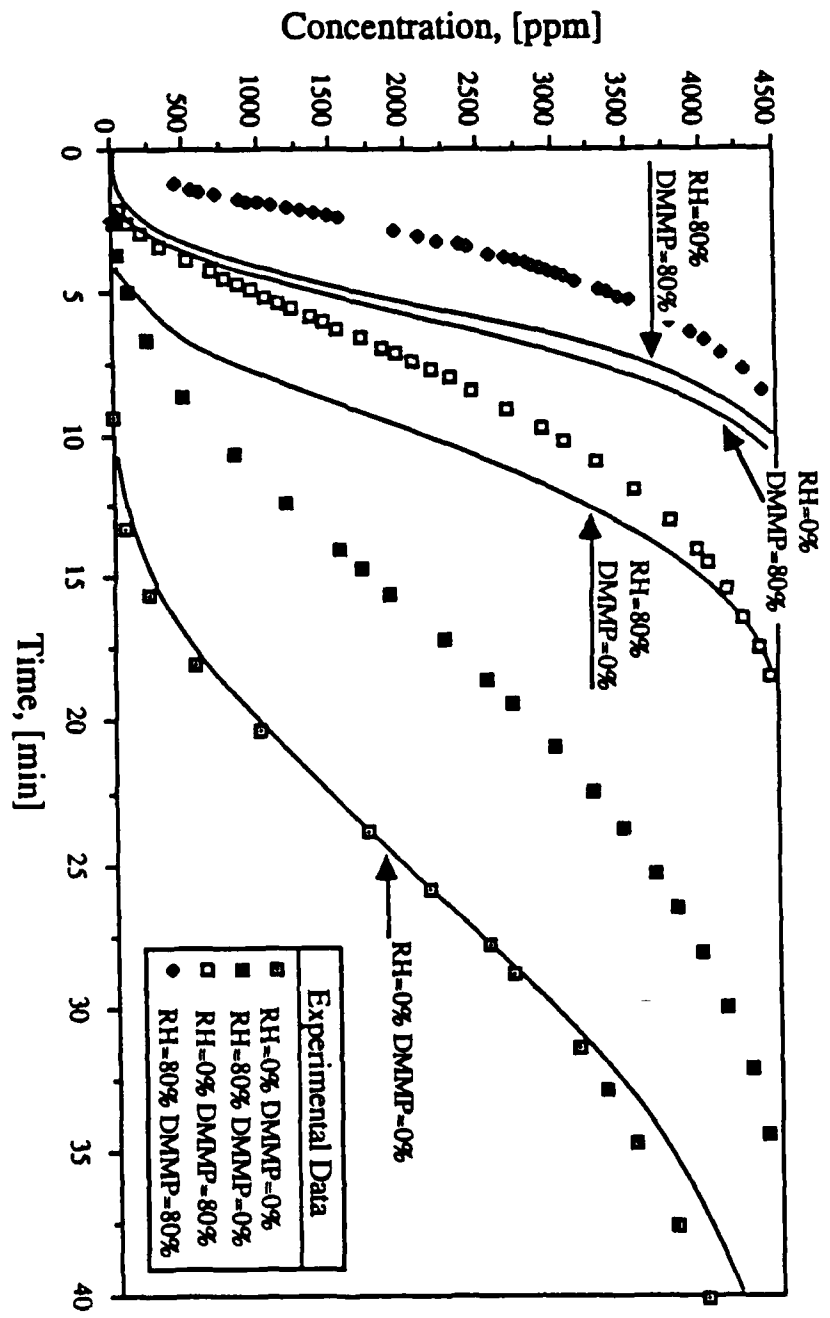


Figure 4.17. Model predictions for breakthrough curves for methanol on a 10 g ASC whetlerite bed (depth=1 cm) at 19.0°C. Flow rate of nitrogen carrier gas is 6.7 liters/min.

4.6 Conclusions.

The determination of residual adsorptive capacity of gas mask cartridges is an important problem. Variables are relative humidity, amount of adsorbed toxins, and the water solubility of the indicator gas. This work has presented a comprehensive study comparing the use of a water-soluble and a non-water-soluble indicator gas over varying conditions of humidity and toxin saturation. Results indicate that a water-soluble indicator counteracts the effect of adsorbed water.

In summary, the conclusions are:

1.) Adsorbed water vapor blocks adsorption sites from indicator gases.

2.) A water-soluble indicator such as methanol is less sensitive to adsorbed water.

3.) Axial dispersion is an important factor in the sharpness of the breakthrough curves.

4.) A model based on Eqn. (4.5) and IAS theory is able to reproduce qualitatively the metnanol breakthrough curves.

4.7 Future Work.

4.7.1 Theory.

The model should be expanded to include an absorption term based on the water solubility of the indicator gas used. By including this cooperative effect in addition to the competitive effects of physical adsorption, a more accurate mathematical description of the physical system can be obtained. Then, predictions can be made for a variety of substances in an effort to minimize the effect of adsorbed water on the retention time of the indicator gas. Optimum combinations of adsorptive strength and water solubility of the indicator can be identified in this manner.

4.7.2 Experiment.

Work should focus on ammonia as a test gas, at higher concentrations than that used in my pulse work. This will circumvent the problems associated with chemisorption while providing the possibility of olfactory detection.

The equipment should be modified as follows to use ammonia as a square-wave input. The thermal conductivity detector should be used to detect ammonia from a helium carrier gas. A square wave input of ammonia injected into the system using a solenoid valve programmed by the Spectra-Physics integrator would allow the delivery of precise quantities. This stream should be superimposed on a flowing helium stream at 20 psig, and the outlet fed directly to the TCD, yielding a continuous output curve of concentration *vs.* time. The helium pressure must be maintained at 20 psig in order to protect the elements in the TCD from burnout which can occur easily at low pressure. Since helium is nonadsorbing under these conditions of temperature and pressure, the higher pressure operation will not affect the results. The GC can be calibrated using previously purchased standards of ammonia in helium. In addition, a stronger water reservoir will need to be constructed to withstand the increased pressure of the system.

With these changes, the existing system can be used to study square-wave inputs of ammonia.

Literature Cited.

Ba(66) Babcock, R. E., D. W. Green and R. H. Perry, "Longitudinal Dispersion Mechanisms in Packed Beds," *AIChE J.*, **12**, 922 (1966).

Ba(77) Bashi, H. and D. Gunn, "The Characterization of Fixed Beds of Porous Solids from Pulse Response", *AIChE Journal*, *23*, 40-48 (1977).

Bi(62) Bischoff, K. B. and O. Levenspiel, "Fluid dispersion-generalization and comparison of mathematical models–I Generalization of models," *Chem. Eng. Sci.*, **17**, 245 (1962).

Bi(62) Bischoff, K. B. and O. Levenspiel, "Fluid dispersion-generalization and comparison of mathematical models–I Comparison of models," *Chem. Eng. Sci.*, **17**, 257 (1962).

Br(78) Brunovska, A., V. Hlavacek, J. Ilavsky and J. Valtyni, "An Analysis of a Nonisothermal One-Component Sorption in a Single Adsorbent Particle," *Chem. Eng. Sci.*, **33**, 1385 (1978).

Ca(81) Caban, R. and T. W. Chapman, "Solution of Boundary-Layer Transport Problems by Orthogonal Collocation," *Chem. Eng. Sci.*, **36**, 849 (1981).

Ch(68) Cheselske, F. J., G. Counas, A. W. Loven and E. D. Tolles, "Evaluation of Fundamental Parameters of Carbon Sorbents," Department of the Army Physical Protection Laboratory, Defense Development and Engineering Laboratories, Edgewood, MD (1968).

Ch(81) Chung, B. and A. Sacco, Jr., "Hydrocarbon Pulse Testing for Collective Filters," Worcester Polytechnic Institute, Dept. of Chem. Eng., July (1981).

de(86) de Lasa, H., J. Hazlett and O. M. Fuller, "Evaluation of the Moment Method Technique for the Definition of Adsorption Parameters in a Packed Bed," *Chem. Eng. Sci.*, **41**, 1233 (1986).

Et(67) Ettre, L. S. and A. Zlatkis, "The Practice of Gas Chromatography," Interscience, Wiley NY (1967).

Gö(86) Göebel, J. C., K. Booij and M. H. Fortuin, "Axial Dispersion in Single-Phase Flow in Pulsed Packed Columns," *Chem. Eng. Sci.*, **41**, 3197 (1986).

Ha(80) Harwell, J. F., A. I. Liapis, R. Litchfield and D. T. Hanson, "A Non-Equilibrium Model for Fixed-Bed Multi-Component Adiabatic Adsorption," *Chem. Eng. Sci.*, **35**, 2287 (1980).

Hi(86) Hills, J. H., "An Investigation of the Linear Driving Force Approximation to Diffusion in Spherical Particles," *Chem. Eng. Sci.*, **41**, 2779 (1986).

Kl(80) Kladnig, W. F., A. H. Weiss and L. A. Jonas, "Non-Destructive Measurement of Residual Adsorption Capacity of Charcoal Filters", *Carbon*, *18* 31-35 (1980).

Ku(65) Kucera, E., "Contribution to the Theory of Chromatography Linear Non-Equilibrium Elution Chromatography," *J. Chromatog.*, **19**, 237 (1965).

La(52) Lapidus, L. and N. R. Amundson, "Mathematics of Adsorption in Beds. VI. The Effect of Longitudinal Diffusion in Ion Exchange and Chromatographic Columns," *J. Phys. Chem.*, **56**, 984 (1952).

Le(63) Levenspiel, O. and K. B. Bischoff, "Patterns of Flow in Chemical Process Vessels" in *Advances in Chemical Engineering*, Ed. T. B. Drew, J. W. Hoopes Jr. and T. Vermeulen, Academic Press, NY 4, 95 (1963).

Me(84) Message, G. M., "Practical Aspects of Gas Chromatography/Mass Spectrometry," Wiley, NY (1984).

Mo(86) Moon, H. and W. K. Lee, "A Lumped Model for Multicomponent Adsorptions in Fixed Beds," *Chem. Eng. Sci.*, **41**, 1995 (1986).

Ne(74) Nelson, G. O. and C. A. Harder, "Respirator Cartridge Efficiency Studies: V. Effect of Solvent Vapor", *American Industrial Hygiene Association Journal*, 391-410 (1974).

Po(74) Ponec, V., Z. Knor and C. Slavoj, "Adsorption on Solids," CRC Press, Cleveland, 472-477 (1974).

Ra(81) Rasmuson, A., "Exact Solution of a Model for Diffusion and Transient Adsorption in Particles and Longitudinal Dispersion in Packed Beds," *AIChE J.*, **27**, 1032 (1981).

Ra(80) Rasmuson, A., "Exact Solution of a Model for Diffusion in Particles and Longitudinal Dispersion in Packed Beds," *AIChE J.*, **26**, 686 (1980).

Ro(52) Rosen, J. B., "Kinetics of a Fixed Bed System for Solid Diffusion into Spherical Particles," *J. Chem. Phys.*, **20**, 387 (1952).

US(84) Commander, U.S. Army Armament, Munitions and Chemical Command AMSMC-TDC-S(A), Aberdeen Proving Ground, MD (1984).

va(56) van Deemter, J. J., F. J. Zuiderweg and A. Klinkenberg, "Longitudinal diffusion and resistance to mass transfer as causes of nonideality in chromatography," *Chem. Eng. Sci.*, **5**, 271 (1956).

Ve(53) Vermeulen, T., "Theory for Irreversible and Constant-Pattern Solid Diffusion," *Ind. Eng. Chem.*, **45**, 1664 (1953).

Wa(78) Wakao, N. and T. Funazkri, "Effect of Fluid Dispersion Coefficients on Particle-to-Fluid Mass Transfer Coefficients in Packed Beds. Correlation of Sherwood Numbers," *Chem. Eng. Sci.*, **33**, 1375 (1978).

Wo(81) Wood, G. O. and F. O. Valdez, "Desorption of Triethylenediamine from Impregnated Respirator Charcoals," *American Ind. Hygiene Conference, Portland, Los Alamos Scientific Laboratory*, (1981).

Ya(87) Yang,R. T., "Gas Separation by Adsorption Processes," Butterworths, Boston, (1974).

Za(45) Zabor, J. W., "Mechanism of Chemical Removal of Gases," Chapter 7 of Vol. 1, Summary Technical Report of Division 10, NRDC. Military Problems with Aerosols and Nonpersistant Gases, (1945).

Appendix E.

Modelling of Pulse-and Step-Change Inputs.

The model used to analyze the data in Chapter 4 was given by Levenspiel [Le(63)] and Bischoff [Bi(62)] as the solution for the breakthrough curve for linear, isothermal, trace component systems. The outlet profile as a function of time, t, is given by

$$\frac{c}{c_o} = \frac{1}{2}\mathrm{erfc}\left\{\frac{1-t/\bar{t}}{2\left[D_L t/(v z \bar{t})\right]^{1/2}}\right\}, \qquad (E.1)$$

where c_o and c are the input and output concentrations, respectively, D_L is the longitudinal dispersion coefficient, z is the bed depth and v is the superficial velocity. The retention time $\bar{t}$ is defined as

$$\bar{t} = \frac{z}{v}\left\{1 + K\left(\frac{1-\epsilon}{\epsilon}\right)\right\} \qquad (E.2)$$

where K is the ratio of concentrations inside and outside the adsorbent and is referred to as a dimensionless Henry's constant, and ϵ is the interparticle void fraction of the bed.

Eqn. (E.1) gives the response to a step change; its differential, (dc/dt), is the response to a pulse input; this is shown in Fig. E.1.

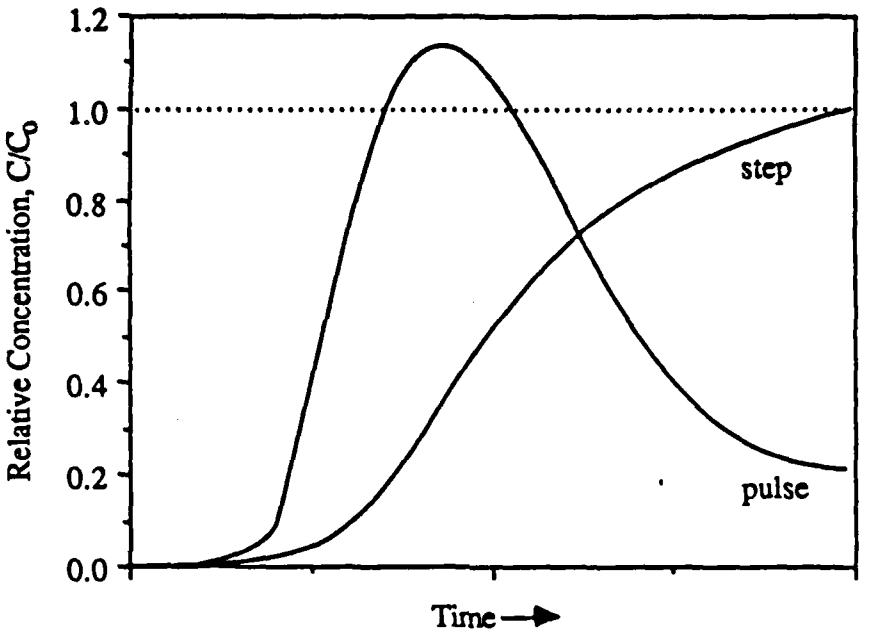
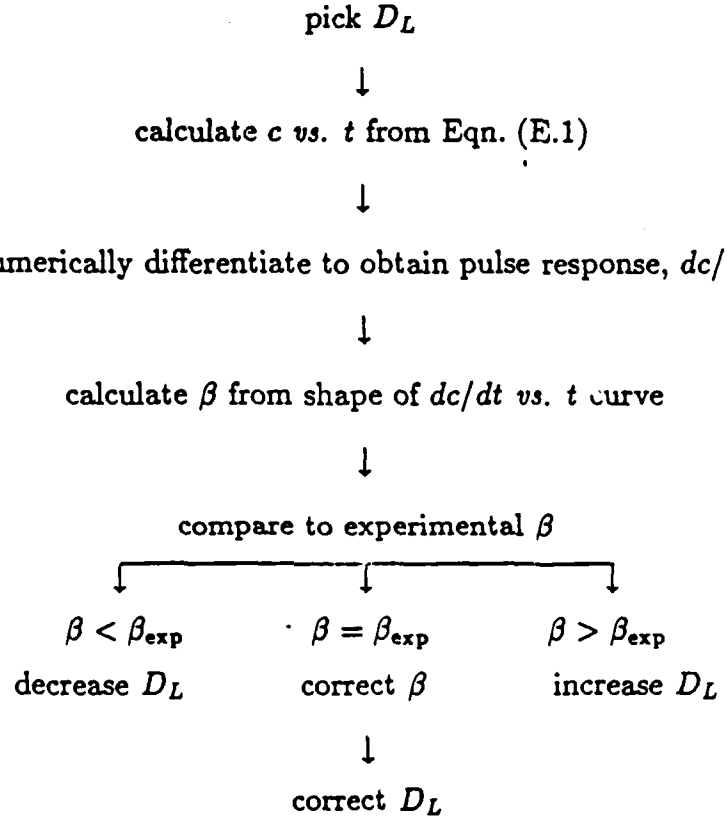


Figure E.1 Response curves from Eqn. (E.1) for pulse and step input.

Calculation of D_L from Pulse Experiments.

The longitudinal dispersion coefficient, (D_L), was calculated from the pulse data. The bed depth, $z = 1$ cm, superficial velocity $v = 6.12$ cm/sec, and the void fraction $\epsilon = 0.43$. The data from pulse experiments were retention time and shape, where the shape is characterized by the parameter β=(peak height)/(peak width). The algorithm for determining D_L is:



As shown in Chapter 4, the calculated values of D_L decrease with increasing loading of DMMP or water for both propane and methanol, but the decrease in D_L for methanol is smaller than that for propane.

Step-Change Response.

Eqn. (E.1), (E.2), and IAS theory [My(65)] were used to model the step-change experiments.

Four combinations of relative humidity (RH) and DMMP loading were used; 0% and 80% RH, and 0% and 80% DMMP saturation. The data for 0% RH and 0% DMMP (see Fig. 4.9) was fit with Eqns. (E.1) and (E.2), and $K_\circ$ and D_L were determined; values are given in Table E.1.

Table E.1. Dimensionless Henry's constant and longitudinal dispersion coefficient obtained from fit of experimental data.

RH%	DMMP%	$K_\circ$	D_L
0	0	8000	0.40

D_L was held constant at 0.40 and IAS theory was used to predict K in the presence of water and DMMP.

IAS theory requires pure-component isotherms for each component; DMMP, water,and methanol. A DMMP isotherm on ASC whetlerite was given by Cheselske *et al.* [Ch(68)]; water on ASC wheterlite was given by Chung and Sacco [Ch(81)]. Both isotherms were obtained from graphs. The DMMP isotherm was fit with the Tóth equation,

$$n = mP(b + P^t)^{-1/t} \qquad (E.3)$$

for P in Torr and n in mmol/g with the parameters m, b, and t given in Table E.2.

Table E.2. Tóth parameters for DMMP on ASC whetlerite.

m	b	t
2.85	0.02025	0.34

The water isotherm on ASC whetlerite is sigmoidal and was fit with a polynomial,

$$n = 0.3874P_r - 2.696P_r^2 + 9.984P_r^3 - 11.91P_r^4 + 4.602P_r^5 \qquad (E.4)$$

where P_r is P/P_{sat} or RH.

No isotherm for methanol on ASC whetlerite was available and attempts to measure this were unsuccessful (see Chapter 2). Methanol adsorption was measured on BPL carbon; the Henry's constant calculated from the Tóth equation was H_o=1.2 mmol/(g-Torr).

Eqns. (E.1) and (E.2) require a value of K; the following equation was assumed to hold:

$$K = \frac{H}{H_o} K_o \qquad (E.5)$$

where K_o=8000, H_o=1.2, and H was calculated from IAS theory using pure-component isotherms for DMMP, water, and methanol. IAS calculations were performed specifying the partial pressure of water and the amount of DMMP adsorbed. Experiments in Chapter 4 indicate that DMMP is negligibly displaced by adsorbing water, so the amount of adsorbed DMMP was assumed invariant. The results are:

Table E.3. Values of K calculated for different combinations of relative humidity and DMMP saturation.

RH, %	DMMP, %	K
80	0	3130
0	80	1520
80	80	1480

These values of K were used with $D_L = 0.40$ in Eqn. (E.1) and (E.2) to produce the curves given in Fig. 4.17.

Literature Cited.

Bi(62) Bischoff, K. B. and O. Levenspiel, "Fluid dispersion-generalization and comparison of mathematical models–I Generalization of models," *Chem. Eng. Sci.*, **17**, 245 (1962).

Bi(62) Bischoff, K. B. and O. Levenspiel, "Fluid dispersion-generalization and comparison of mathematical models–I Comparison ot models," *Chem. Eng. Sci.*, **17**, 257 (1962).

Ch(68) Cheselske, F. J., G. Counas, A. W. Loven and E. D. Tolles, "Evaluation of Fundamental Parameters of Carbon Sorbents," Department of the Army Physical Protection Laboratory, Defense Development and Engineering Laboratories, Edgewood, MD (1968).

Ch(81) Chung, B. and A. Sacco, Jr., "Hydrocarbon Pulse Testing for Collective Filters," Worcester Polytechnic Institute, Dept. of Chem. Eng., July (1981).

Le(63) Levenspiel, O. and K. B. Bischoff, "Patterns of Flow in Chemical Process Vessels" in *Advances in Chemical Engineering*, Ed. T. B. Drew, J. W. Hoopes Jr. and T. Vermeulen, Academic Press, NY 4, 95 (1963).